CLAIMS

1. A method for preparing a ruthenium carbene complex precursor comprising:

reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate; and

reacting the ruthenium intermediate with an L-type ligand to form the ruthenium carbene complex precursor.

2. The invention of claim 1 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.

~~3. The invention of claim 1 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, and a combination thereof.~~

43. The invention of claim 1 wherein the L-type ligand comprises a cyclic olefin.

~~5. The invention of claim 4 wherein the cyclic olefin is selected from the group consisting of a diene, a triene, and a combination thereof.~~

~~6~~4. The invention of claim 43 wherein the cyclic olefin is selected from the group consisting of cyclohexadiene, cycloheptadiene, cyclooctadiene, cyclononadiene, cyclodecadiene, cycloundecadiene, cyclododecadiene, cyclododecatriene, paramenthadiene, phellandrene, norbornadiene, terpinene, limonene, and combinations thereof.

~~7. The invention of claim 4 wherein the cyclic olefin is selected from the group consisting of cyclooctadiene, cyclododecatriene, and combinations thereof.~~

~~8. The invention of claim 4 wherein the cyclic olefin comprises cyclooctadiene.~~

~~9~~5. The invention of claim 1 wherein the L-type ligand comprises a phosphorous-containing ligand having a structure $PR^1R^2R^3$;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryioxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

~~106~~. The invention of claim ~~95~~ wherein the phosphorous-containing ligand comprises triphenyl phosphine.

~~117~~. The invention of any of claims 1 to ~~106~~ wherein the hydrogen halide is selected from the group consisting of hydrogen chloride, hydrogen bromide, and a combination thereof.

~~12. The invention of any of claims 1 to 10 wherein the hydrogen halide comprises hydrogen chloride.~~

~~13. The invention of any of claims 1 to 10 wherein the hydrogen halide comprises hydrogen bromide.~~

~~14. The invention of any of claims 1 to 10 wherein the hydrogen halide comprises hydrogen chloride and wherein the L-type ligand comprises a cyclic olefin.~~

~~15. The invention of claim 14 wherein the cyclic olefin comprises cyclooctadiene.~~

~~168~~. The invention of any of claims 1 to ~~106~~ wherein the ruthenium refinery salt comprises a material selected from the group consisting of $(NH_4)_2RuCl_5$, $(NH_4)_2RuCl_5.H_2O$, polyhydrated $(NH_4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof.

~~17. The invention of claim 16 wherein the ruthenium refinery salt further comprises NH_4Cl.~~

~~18. The invention of claim 17 wherein the method further comprises removing at least a portion of the NH_4Cl from the ruthenium refinery salt prior to reacting the ruthenium refinery salt with the hydrogen halide.~~

~~19. The invention of claim 18 wherein at least a portion of the NH_4Cl is removed via sublimation.~~

~~20. The invention of claim 19 wherein at least a portion of sublimed NH_4Cl is removed from the ruthenium refinery salt prior to reacting the ruthenium refinery salt with the hydrogen halide.~~

~~21~~9. The invention of any of claims 1 to ~~10~~6 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of halide ligands.

~~22. The invention of any of claims 1 to 10 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of chloride ligands.~~

~~23. The invention of claim 22 wherein the ruthenium intermediate further comprises one or a plurality of additional halide ligands other than chloride.~~

~~24~~10. The invention of claim 1 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$.

~~25. The invention of claim 24 wherein at least a portion of the $(NH_4)_2RuCl_6$ is crystalline.~~

~~26. The invention of claim 24 wherein at least a portion of the $(NH_4)_2RuCl_6$ is a powder.~~

27. The invention of claim 12 wherein the hydrogen chloride is provided in aqueous solution as hydrochloric acid.

28. The invention of claim 27 wherein concentration of the hydrochloric acid is at least about 5 M or higher.

29. The invention of claim 27 wherein concentration of the hydrochloric acid is at least about 6 M or higher.

30. The invention of claim 6 wherein the reacting with the hydrogen halide comprises a hydrothermal treatment.

31. The invention of claim 24 wherein the hydrogen halide comprise hydrogen chloride, which is provided in aqueous solution as hydrochloric acid having a concentration of at least about 6M, and wherein the reacting is performed in a closed system.

32. The invention of claim 31 wherein a reaction temperature in the closed system is at least about 100 °C.

33. The invention of claim 32 wherein at least a portion of the $(NH_4)_2RuCl_6$ is crystalline.

34. The invention of claim 6 wherein the reacting with the hydrogen halide comprises atmospheric conditions.

35. The invention of claim 34 wherein the hydrogen halide comprises hydrogen chloride, which is provided in aqueous solution as concentrated hydrochloric acid, and wherein the reacting is performed in an open system.

36. The invention of claim 35 wherein the ruthenium refinery salt is refluxed in the concentrated hydrochloric acid.

~~37. The invention of claim 36 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$, and wherein at least a portion of the $(NH_4)_2RuCl_6$ is a powder.~~

~~38. The invention of claim 15 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$, and wherein the cyclooctadiene comprises *cis, cis*-1,5-cyclooctadiene.~~

~~39. The invention of claim 15 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$ and wherein the reacting of the ruthenium intermediate with cyclooctadiene comprises refluxing the ruthenium intermediate and *cis, cis*-1,5-cyclooctadiene in ethanol.~~

~~40. The invention of any of claims 1 to 10 wherein the ruthenium carbene complex precursor comprises a material having a structure $[RuCl_2(COD)]_x$, wherein x is an integer value of 1 or more.~~

~~41. The invention of any of claims 1 to 10 wherein the ruthenium carbene complex precursor comprises a material having a structure $RuCl_2(PR^1R^2R^3)_3$;~~

~~wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{40} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{40} alkoxy, and combinations thereof; and~~

~~wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.~~

4211. A method for preparing a ruthenium carbene complex precursor comprising:

reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate; and

reacting the ruthenium intermediate with cyclooctadiene and/or a phosphorous-containing material having a structure $PR^1R^2R^3$ to form the ruthenium carbene complex precursor;

wherein the ruthenium refinery salt comprises a material selected from the group consisting of $(NH_4)_2RuCl_5$, $(NH_4)_2RuCl_5.H_20$, polyhydrated $(NH4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof;

wherein the ruthenium intermediate comprises a compound selected from the group consisting of $(NH_4)_2RuX^16$, $(NH_4)2RuX^1{}_yX^2{}_{6-y}$, and a combination thereof;

wherein the ruthenium carbene complex precursor comprises a compound having a structure $[RuX^3X^4(COD)]_x$; and/or a compound having a structure $RuX^5X^6(PR^1R^2R^3)_3$;

wherein x is an integer value of 1 or more;

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I with a caveat that X^1 and X^2 are different;

wherein y is an integer value from 1 to 5;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

~~43. A method for preparing a ruthenium vinylcarbene complex comprising: converting a ruthenium carbene complex precursor prepared according to the method of claim 4 into a ruthenium hydrido halide complex; and~~

~~reacting the ruthenium hydrido halide complex with a propargyl halide to form the ruthenium vinylcarbene complex.~~

~~44. The invention of claim 43 wherein the converting comprises reacting the ruthenium carbene complex precursor with a trialkyl phosphine, hydrogen, and a trialkyl amine.~~

45. The invention of claim 43 wherein the ruthenium hydrido halide complex comprises a compound having a structure $[Ru(H)(H_2)X(PR^1R^2R^3)_2]$;

wherein X is a halide;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphoreus is formed.

46. The invention of claim 43 wherein the ruthenium hydrido halide complex comprises a compound having a structure $[Ru(H)(H_2)Cl(PCy_3)_2]$, and wherein the propargyl halide comprises 3-chloro-3-methyl-1-butyne.

47. The invention of claim 46 wherein the ruthenium vinylcarbene complex comprises a compound having a structure $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}C(CH_3)_2$.

48. The invention of claim 44 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an N-heterocyclic carbene ligand.

49. The invention of claim 44 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium vinylcarbene complex.

50. The invention of claim 49 wherein the imidazolidine-containing ruthenium vinylcarbene complex constitutes a second-generation Grubbs-type olefin metathesis catalyst.

51. The invention of claim 49 wherein the imidazolidine ligand comprises 1,3-dimesityl-4,5-dihydroimidazoie.

52. A method for preparing a ruthenium carbene complex comprising:

converting a ruthenium carbene complex precursor prepared according to the method of claim 9 into a ruthenium carbene complex having a structure $(PR^1R^2R^3)_2X^1X^2Ru=CH-R^4$;

wherein X^1 and X^2 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I;

wherein R^1, R^2, R^3, and R^4 are alike or different, and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{40} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{40} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

53. The invention of claim 52 wherein the ruthenium carbene complex precursor comprises a structure $RuCl_2(PR^1R^2R^3)_3$.

54. The invention of claim 52 wherein each of R^1, R^2, R^3, and R^4 comprises phenyl.

55. The invention of claim 52 wherein the converting comprises reacting the ruthenium carbene complex precursor with phenyldiazomethane.

56. The invention of any of claims 52 to 55 further comprising replacing a phosphorous-containing ligand of the ruthenium carbene complex with an N-heterocyclic carbene ligand to form an N-heterocyclic carbene-containing ruthenium carbene complex.

57. The invention of any of claims 52 to 55 further comprising replacing a phosphorous-containing ligand of the ruthenium carbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium carbene complex.

58. A method for preparing a ruthenium complex comprising reacting a ruthenium refinery salt with a hydrogen halide to form the ruthenium complex.

59. The invention of claim 58 wherein the ruthenium complex comprises an $[RuX^1_yX^2_{6-y}]^{2-}$ anion, wherein X^1 and X^2 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I, and wherein y is an integer value from 1 to 6.

60. The invention of claim 58 wherein the ruthenium complex comprises one or a plurality of ammonium cations and one or a plurality of halide ligands.

61. The invention of claim 58 wherein the ruthenium complex comprises one or a plurality of ammonium cations and one or a plurality of chloride ligands.

62. The invention of claim 58 wherein the ruthenium complex comprises a compound selected from the group consisting of $(NH_4)_2RuX^1_6$, $(NH_4)_2RuX^1_yX^2_{6-y}$, and a combination thereof; wherein X^1 and X^2 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I; and wherein y is an integer value from 1 to 5.

63. The invention of claim 58 wherein the ruthenium complex comprises a compound selected from the group consisting of $(NH_4)_2RuCl_6$, $(NH_4)_2RuBr_6$, $(NH_4)_2RuCl_zBr_{6-z}$ wherein z is an integer from 1 to 5, and combinations thereof.

64. The invention of claim 58 wherein the hydrogen halide is selected from the group consisting of hydrogen chloride, hydrogen bromide, and a combination thereof.

65. The invention of claim 58 wherein the hydrogen halide comprises hydrogen chloride.

66. The invention of claim 58 wherein the hydrogen halide comprises hydrogen bromide.

~~67. The invention of claim 58 wherein the ruthenium refinery salt comprises a material selected from the group consisting of $(NH_4)_2RuCl_5$, $(NH_4)_2RuCl_5.H_2O$, polyhydrated $(NH_4)_2RuCl_5$, $(NH_4)_4Ru_2OCl_{10}$, and combinations thereof.~~

~~68. The invention of claim 67 wherein the hydrogen chloride is provided in aqueous solution as hydrochloric acid.~~

~~69. The invention of claim 58 wherein the reacting with the hydrogen halide comprises a hydrothermal treatment.~~

~~70. The invention of claim 58 wherein the reacting with the hydrogen halide comprises atmospheric conditions.~~

~~71~~12. A method of preparing a MX_2L_q complex comprising:

reacting a ruthenium (IV) hexahalo complex that comprises a $[RuX^1_yX^2_{6-y}]^-$ anion with an L-type ligand;

wherein M comprises ruthenium;

wherein X^1 and X^2 are halogen atoms that are independently selected from the group consisting of F, Cl, Br, and I; and

wherein y is an integer value from 1 to 6.

~~72~~13. The invention of claim ~~71~~12 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.

~~73. The invention of claim 71 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, and a combination thereof.~~

~~74~~14. The invention of claim ~~71~~12 wherein the L-type ligand comprises a cyclic olefin.

~~75. The invention of claim 74 wherein the cyclic olefin is selected from the group consisting of a diene, a triene, and a combination thereof.~~

7615. The invention of claim 7414 wherein the cyclic olefin is selected from the group consisting of cyclohexadiene, cycioheptadiene, cyciooctadiene, cyclononadiene, cyclodecadiene, cycloundecadiene, cyclododecadiene, cyclododecatriene, paramenthadiene, phellandrene, norbornadiene, terpinene, limonene, and combinations thereof.

~~77. The invention of claim 74 wherein the cyclic olefin is selected from the group consisting of cyciooctadiene, cyclododecatriene, and combinations thereof.~~

7816. The invention of claim 7414 wherein the cyclic olefin comprises 1,5-cyclooctadiene.

7917. The invention of claim 7112 wherein the L-type ligand comprises a phosphorous-containing ligand having a structure $PR^1R^2R^3$;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

8018. The invention of claim 7917 wherein the phosphorous-containing ligand comprises triphenyi phosphine.

8119. The invention of any of claims 7112 to 8018 wherein the hydrogen halide is selected from the group consisting of hydrogen chloride, hydrogen bromide, and a combination thereof.

~~82. A method for preparing a ruthenium carbene complex precursor comprising: reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate; and~~

reacting the ruthenium intermediate with an L-type ligand and a reducing agent to form the ruthenium carbene complex precursor.

83. The invention of claim 82 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.

84. The invention of claim 82 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, and a combination thereof.

85. The invention of claim 82 wherein the L-type ligand comprises a cyclic olefin.

86. The invention of claim 85 wherein the cyclic olefin is selected from the group consisting of a diene, a triene, and a combination thereof.

87. The invention of claim 85 wherein the cyclic olefin is selected from the group consisting of cyclohexadiene, cycloheptadiene, cyclooctadiene, cyclononadiene, cyclodecadiene, cycloundecadiene, cyclododecadiene, cyclododecatriene, paramenthadiene, phellandrene, norbornadiene, terpinene, limonene, and combinations thereof.

88. The invention of claim 85 wherein the cyclic olefin is selected from the group consisting of cyclooctadiene, cyclododecatriene, and combinations thereof.

89. The invention of claim 85 wherein the cyclic olefin comprises cyclooctadiene.

90. The invention of claim 82 wherein the L-type ligand comprises a phosphorous-containing ligand having a structure $PR^1R^2R^3$;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{40} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{40} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

91. The invention of claim 90 wherein the phosphorous-containing ligand comprises triphenyl phosphine.

92. The invention of claim 82 wherein the hydrogen halide is selected from the group consisting of hydrogen chloride, hydrogen bromide, and a combination thereof.

93. The invention of claim 82 wherein the hydrogen halide comprises hydrogen chloride.

94. The invention of claim 82 wherein the hydrogen halide comprises hydrogen bromide.

95. The invention of claim 82 wherein the hydrogen halide comprises hydrogen chloride and wherein the L-type ligand comprises a cyclic olefin.

96. The invention of claim 95 wherein the cyclic olefin comprises cyclooctadiene.

97. The invention of claim 82 wherein the ruthenium refinery salt comprises a material selected from the group consisting of $(NH_4)_2RuCl_5$, $(NH_4)_2RuCl_5.H_2O$, polyhydrated $(NH_4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof.

98. The invention of claim 97 wherein the ruthenium refinery salt further comprises NH_4Cl.

99. The invention of claim 98 wherein the method further comprises removing at least a portion of the NH_4Cl from the ruthenium refinery salt prior to reacting the ruthenium refinery salt with the hydrogen halide.

100. The invention of claim 99 wherein at least a portion of the NH_4Cl is removed via sublimation.

101. The invention of claim 100 wherein at least a portion of sublimed NH_4Cl is removed from the ruthenium refinery salt prior to reacting the ruthenium refinery salt with the hydrogen halide.

102. The invention of claim 99 wherein at least a portion of the NH_4Cl is removed via washing with water.

103. The invention of claim 99 wherein at least a portion of the NH_4Cl is removed via washing with an alcohol.

104. The invention of claim 103 wherein the alcohol comprises ethanol.

105. The invention of claim 99 wherein at least a portion of the NH_4Cl is removed via Soxhlet extraction with an alcohol.

106. The invention of claim 82 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of halide ligands.

107. The invention of claim 82 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of chloride ligands.

108. The invention of claim 107 wherein the ruthenium intermediate further comprises one or a plurality of additional halide ligands other than chloride.

109. The invention of claim 82 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$.

110. The invention of claim 109 wherein at least a portion of the $(NH4)_2RuCl_6$ is crystalline.

111. The invention of claim 109 wherein at least a portion of the $(NH_4)_2RuCl_6$ is a powder.

112. The invention of claim 93 wherein the hydrogen chloride is provided in aqueous solution as hydrochloric acid.

113. The invention of claim 112 wherein concentration of the hydrochloric acid is at least about 5 M or higher.

114. The invention of claim 112 wherein concentration of the hydrochloric acid is at least about 6 M or higher.

115. The invention of claim 87 wherein the reacting with the hydrogen halide comprises a hydrothermal treatment.

116. The invention of claim 109 wherein the hydrogen halide comprise hydrogen chloride, which is provided in aqueous solution as hydrochloric acid having a concentration of at least about 6M, and wherein the reacting is performed in a closed system.

117. The invention of claim 116 wherein a reaction temperature in the closed system is at least about 100 °C.

118. The invention of claim 117 wherein at least a portion of the $(NH_4)_2RuCl_6$ is crystalline.

119. The invention of claim 87 wherein the reacting with the hydrogen halide comprises atmospheric conditions.

120. The invention of claim 119 wherein the hydrogen halide comprises hydrogen chloride, which is provided in aqueous solution as concentrated hydrochloric acid, and wherein the reacting is performed in an open system.

121. The invention of claim 120 wherein the ruthenium refinery salt is refluxed in the concentrated hydrochloric acid.

122. The invention of claim 121 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$, and wherein at least a portion of the $(NH_4)_2RuCl_6$ is a powder.

123. The invention of claim 96 wherein the ruthenium intermediate comprises a Gompound having a structure $(NH_4)_2RuCl6$, and wherein the cyclooctadiene comprises *cis, cis*-1,5-cyclooctadiene.

124. The invention of claim 96 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$, and wherein the reacting of the ruthenium intermediate with cyclooctadiene comprises refluxing the ruthenium intermediate and *cis, cis*-1,5-cyclooctadiene in ethanol.

125. The invention of claim 82 wherein the reducing agent is inorganic.

126. The invention of claim 82 wherein the reducing agent comprises a metal.

127. The invention of claim 126 wherein the metal is selected from the group consisting of Group 7 elements, Group 8 elements, Group 9 elements, Group 10 elements, Group 11 elements, and combinations thereof.

128. The invention of claim 82 wherein the reducing agent comprises $FeCl_2$ and/or a hydrated form thereof.

129. The invention of claim 82 wherein the reducing agent comprises $CoCl_2$ and/or a hydrated form thereof.

130. The invention of claim 82 wherein the reducing agent is organic.

131. The invention of claim 82 wherein the reducing agent is present at a loading of at least about 1 molar equivalent.

132. The invention of claim 82 wherein the reacting of the ruthenium intermediate with the L-type ligand and the reducing agent is performed in an alcoholic solvent.

133. The invention of claim 132 wherein the alcoholic solvent comprises ethanol.

134. The invention of claim 132 wherein the reacting of the ruthenium intermediate with the L-type ligand and the reducing agent comprises a reaction time of at least about 5 hours.

135. The invention of claim 134 wherein the reaction time is at least about 10 hours.

136. The invention of claim 134 wherein the reaction time is at least about 15 hours.

137. The invention of claim 134 wherein the reaction time is at least about 20 hours.

138. The invention of claim 82 wherein the reducing agent comprises $FeCl_2$, and wherein the L-type ligand comprises a cyclic olefin.

139. The invention of claim 138 wherein the cyclic olefin comprises cyclooctadiene.

140. The invention of claim 82 wherein the ruthenium carbene complex precursor comprises a material having a structure $[RuCl_2(COD)]_x$, wherein x is an integer value of 1 or more.

141. The invention of claim 82 wherein the ruthenium carbene complex precursor comprises a material having a structure $RuCl_2(PR^1R^2R^3)_3$;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

142. A method for preparing a ruthenium carbene complex precursor comprising: reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate; and

reacting the ruthenium intermediate with (a) cyclooctadiene and/or a phosphorous-containing material having a structure $PR^1R^2R^3$ and (b) a reducing agent to form the ruthenium carbene complex precursor;

wherein the ruthenium refinery salt comprises a material selected from the group consisting of $(NH_4)_2RuCl_6$, $(NH_4)_2RuCl_5.H_2O$, polyhydrated $(NH_4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof;

wherein the ruthenium intermediate comprises a compound selected from the group consisting of $(NH_4)_2RuX^1_6$, $(NH_4)_2RuX^1_yX^2_{6-y}$, and a combination thereof;

wherein the reducing agent comprises a metal selected from the group consisting of Group 7 elements, Group 8 elements, Group 9 elements, Group 10 elements, Group 11 elements, and combinations thereof;

wherein the ruthenium carbene complex precursor comprises a compound having a structure $[RuX^3X^4(COD)]_x$ and/or a compound having a structure $RuX^5X^6(PR^1R^2R^3)_3$;

wherein x is an integer value of 1 or more;

wherein X^1, X^2, X^3, X^4, X^5, and X^6 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I with a caveat that X^1 and X^2 are different;

wherein y is an integer value from 1 to 5;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or

unsubstituted aryl, substituted or unsubstituted C_1-C_{40} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{40} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

143. The invention of claim 142 wherein the reducing agent is selected from the group consisting of $FeCl_2$, $CoCl_2$, hydrated forms thereof, and combinations thereof.

144. A method for preparing a ruthenium vinylcarbene complex comprising:
converting a ruthenium carbene complex precursor prepared according to the method of claim 4 into a ruthenium hydrido halide complex; and

reacting the ruthenium hydrido halide complex with a propargyl halide to form the ruthenium vinylcarbene complex.

145. The invention of claim 144 wherein the converting comprises reacting the ruthenium carbene complex precursor with a trialkyl phosphine, hydrogen, and a trialkyl amine.

146. The invention of claim 144 wherein the ruthenium hydrido halide complex comprises a compound having a structure $[Ru(H)(H_2)X(PR^1R^2R^3)_2]$;

wherein X is a halide;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{40} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{40} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

147. The invention of claim 144 wherein the ruthenium hydrido halide complex comprises a compound having a structure $[Ru(H)(H_2)Cl(PCy_3)_2]$,

and wherein the propargyl halide comprises 3-chloro-3~methyl-1-butyne.

148. The invention of claim 147 wherein the ruthenium vinylcarbene complex comprises a compound having a structure $(PCy_3)_2Cl_2Ru=CH-CH=C(CH_3)_2$.

149. The invention of claim 145 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an N-heterocyclic carbene ligand.

150. The invention of claim 145 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium vinylcarbene complex.

151. The invention of claim 150 wherein the imidazolidine-containing ruthenium vinylcarbene complex constitutes a second-generation Grubbs-type olefin metathesis catalyst.

152. The invention of claim 150 wherein the imidazolidine ligand comprises 1,3-dimesityl-4,5~dihydroimidazole.

153. A method for preparing a ruthenium carbene complex comprising:
converting a ruthenium carbene complex precursor prepared according to the method of claim 9 into a ruthenium carbene complex having a structure $(PR^1R^2R^3)_2X^1X^2Ru=CH-R^4$;

wherein X^1 and X^2 are halogen atoms that are each independently selected from the group consisting of F, Cl, Br, and I;

wherein R^1, R^2, R^3, and R^4 are alike or different, and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

154. The invention of claim 153 wherein the ruthenium carbene complex precursor comprises a structure $RuCl_2(PR^1R^2R^3)_3$.

155. The invention of claim 153 wherein each of R^1, R^2, R^3, and R^4 comprises phenyl.

156. The invention of claim 153 wherein the converting comprises reacting the ruthenium carbene complex precursor with phenyldiazomethane.

157. The invention of claim 153 further comprising replacing a phosphorous-containing ligand of the ruthenium carbene complex with an N-heterocyclic carbene ligand to form an N-heterocyclic carbene-containing ruthenium carbene complex.

158. The invention of claim 153 further comprising replacing a phosphorous-containing ligand of the ruthenium carbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium carbene complex.

159. A method of preparing an MX_2L_q complex comprising:
reacting a ruthenium (IV) hexahalo complex that comprises a $[RuX^1_yX^2_{6-y}]^{2-}$ anion with an L-type ligand and a reducing agent;

wherein M comprises ruthenium;
wherein X^1 and X^2 are halogen atoms that are independently selected from the group consisting of F, Cl, Br, and I; and wherein y is an integer value from 1 to 6.

160. The invention of claim 159 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.

161. The invention of claim 159 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, and a combination thereof.

162. The invention of claim 159 wherein the L-type ligand comprises a cyclic olefin.

163. The invention of claim 162 wherein the cyclic olefin is selected from the group consisting of a diene, a triene, and a combination thereof.

164. The invention of claim 162 wherein the cyclic olefin is selected from the group consisting of cyclohexadiene, cycloheptadiene, cyclooctadiene, cyclononadiene, cyclodecadiene, cycloundecadiene, cyclododecadiene, cyclododecatriene, paramenthadiene, phellandrene, norbornadiene, terpinene, limonene, and combinations thereof.

165. The invention of claim 162 wherein the cyclic olefin is selected from the group consisting of cyclooctadiene, cyclododecatriene, and combinations thereof.

166. The invention of claim 162 wherein the cyclic olefin comprises 1,5-cyclooctadiene.

167. The invention of claim 159 wherein the L-type ligand comprises a phosphorous-containing ligand having a structure $PR^1R^2R^3$;

wherein R^1, R^2, and R^3 are alike or different and are each independently selected from the group consisting of substituted or unsubstituted aryl, substituted or unsubstituted C_1-C_{10} alkyl, substituted or unsubstituted aryloxy, substituted or unsubstituted C_1-C_{10} alkoxy, and combinations thereof; and

wherein covalent bonds may optionally exist between two or more of R^1, R^2, and R^3 and/or two of R^1, R^2, and R^3 taken together may optionally form a ring with phosphorous.

168. The invention of claim 167 wherein the phosphorous-containing ligand comprises triphenyl phosphine.

169. The invention of claim 159 wherein the reducing agent is inorganic.

170. The invention of claim 159 wherein the reducing agent comprises a metal.

171. The invention of claim 170 wherein the metal is selected from the group consisting of Group 7 elements, Group 8 elements, Group 9 elements, Group 10 elements, Group 11 elements, and combinations thereof.

172. The invention of claim 159 wherein the reducing agent comprises $FeCl_2$ and/or a hydrated form thereof.

173. The invention of claim 159 wherein the reducing agent comprises $CoCl_2$ and/or a hydrated form thereof.

174. The invention of claim 159 wherein the reducing agent is organic.

175. The invention of claim 159 wherein the reducing agent is present at a loading of at least about 1 molar equivalent.

176. The invention of claim 159 wherein the reacting of the ruthenium intermediate with the L-type ligand and the reducing agent is performed in an alcoholic solvent.

177. The invention of claim 176 wherein the alcoholic solvent comprises ethanol.

178. The invention of claim 176 wherein the reacting of the ruthenium intermediate with the L-type ligand and the reducing agent comprises a reaction time of at least about 5 hours.

179. The invention of claim 178 wherein the reaction time is at least about 10 hours.

180. The invention of claim 178 wherein the reaction time is at least about 15 hours.

181. The invention of claim 178 wherein the reaction time is at least about 20 hours.

~~182. The invention of claim 159 wherein the reducing agent comprises $FeCl_2$, and wherein the L-type ligand comprises a cyclic olefin.~~

~~183. The invention of claim 182 wherein the cyclic olefin comprises cyclooctadiene.~~

~~184. The invention of claim 159 wherein the ruthenium (IV) hexahalo complex further comprises an ammonium cation and wherein y is 6.~~

~~185. The invention of claim 159 wherein the ruthenium (IV) hexahalo complex comprises $(NH_4)_2RuCl_6$.~~

20. The invention of any one of claims 1 to 6 wherein the ruthenium refinery salt is a halogen-containing ruthenium complex.