preparations of $[RuCl_2(COD)]_x$ and $RuCl_2(PPh_3)_3$ via the intermediacy of ruthenium trichloride are costly and inefficient.

[0006] A more efficient and less costly preparation of $[RuCl_2(COD)]_x$, $RuCl_2(PPh_3)_3$, and analogous MX_2L_q ruthenium carbene complex precursors from ruthenium refinery salts—particularly one that does not require the intermediacy of ruthenium metal and/or ruthenium trichloride—is desirable.

SUMMARY

[0007] The scope of the present disclosure is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

[0008] By way of introduction, a first method for preparing a ruthenium carbene complex precursor in accordance with the present teachings includes (a) reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate, and (b) reacting the ruthenium intermediate with an L-type ligand to form the ruthenium carbene complex precursor.

[0008a] In a first aspect, there is provided a method for preparing a ruthenium carbene complex precursor comprising:

(a) reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate, the ruthenium refinery salt being a salt of a halogen-containing ruthenium complex; wherein the hydrogen halide comprises hydrogen chloride, hydrogen bromide, or combinations thereof; and wherein the halogen-containing ruthenium complex comprises halogen atoms selected from the group consisting of chlorine and bromine; and

(b) reacting the ruthenium intermediate with an L-type ligand to form the ruthenium carbene complex precursor,

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

[0008b] In a second aspect, there is provided 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 $(NH_4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof; wherein the ruthenium intermediate comprises a compound selected from the group consisting of $(NH_4)_2RuX^16$, $(NH_4)2RuX^1_yX^2_{6-y}$, 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

integer value from 1 to 6. The M includes ruthenium. X^1 and X^2 are halogen atoms that are independently selected from the group consisting of F, Cl, Br, and I.

[0016a] In another aspect, there is provided a method for preparing a ruthenium complex comprising reacting a ruthenium refinery salt with a hydrogen halide to form the ruthenium complex; wherein the hydrogen halide comprises hydrogen chloride, hydrogen bromide, or combinations thereof; ~~and~~ wherein the halogen-containing ruthenium complex comprises halogen atoms selected from the group consisting of chlorine and bromine; and 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.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 shows a synthetic scheme for converting ruthenium refinery salts to $[RuCl_2(COD)]_x$ and $RuCl_2(PPh_3)_3$ by conventional methodologies.

[0018] FIG. 2 shows a synthetic scheme for converting ruthenium refinery salts to $[RuCl_2(COD)]_x$ in accordance with the present teachings.

[0019] FIG. 3 shows a synthetic scheme for converting the ruthenium carbene complex precursor $[RuCl_2(COD)]_x$ to a ruthenium carbene compound for use as an olefin metathesis catalyst.

[0020] FIG. 4 shows a synthetic scheme for converting ruthenium refinery salts to $RuCl_2(PPh_3)_3$ in accordance with the present teachings.

[0021] FIG. 5 shows a synthetic scheme for converting the ruthenium carbene complex precursor $RuCl_2(PPh_3)_3$ to a ruthenium carbene compound for use as an olefin metathesis catalyst.

[0022] FIG. 6 shows the infrared spectra of (a) $[RuCl_2(COD)]_x$ prepared from the reaction of (NH4)^RuCl6 and cis, cis-1,5-COD (top spectrum), and (b) commercially available $[RuCl_2(COD)]_x$ purchased from Strem Chemicals, Inc. (bottom spectrum).

[0023] FIG. 7 shows the infrared spectra of (a) $[RuCl_2(COD)]_x$ prepared from the reaction of $(NH_4)_2RuCl_6$, cis,cis-1,5-COD, and $FeCl_2$ reducing agent (top spectrum), and (b) commercially available $[RuCl_2(COD)]_x$ purchased from Strem Chemicals, Inc. (bottom spectrum).

DETAILED DESCRIPTION

[0024] A facile synthetic route to ruthenium carbene complex metathesis catalyst precursors—such as $[RuCl_2(COD)]_x$, $RuCl_2(PPh_3)_3$, and analogous MX_2L_q complexes (e.g., where q is an integer from 1 through 4)—has been discovered and is described herein. As shown in FIGS. 2 and 4, the inventive route starts from low-cost ruthenium refinery salts and does not require any conversion of these salts to ruthenium metal or subsequent oxidation of ruthenium metal to $RuCl_3$—two of the principal drawbacks associated with the conventional synthetic preparations of $RuCl_2(COD)]_x$, $RuCl_2(PPh_3)_3$, and analogous complexes.

CLAIMS

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

(a) reacting a ruthenium refinery salt with a hydrogen halide to form a ruthenium intermediate, the ruthenium refinery salt being a salt of a halogen-containing ruthenium complex; wherein the hydrogen halide comprises hydrogen chloride, hydrogen bromide, or combinations thereof; and wherein the halogen-containing ruthenium complex comprises halogen atoms selected from the group consisting of chlorine and bromine; and

(b) reacting the ruthenium intermediate with an L-type ligand to form the ruthenium carbene complex precursor,

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

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.

4. 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. The invention of claim 4 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. 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 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.

10. The invention of claim 9 wherein the phosphorous-containing ligand comprises triphenyl phosphine.

11. The invention of claim 1 wherein the hydrogen halide comprises hydrogen chloride.

12. The invention of claim 1 wherein the hydrogen halide comprises hydrogen bromide.

13. The invention of claim 1 wherein the hydrogen halide comprises hydrogen chloride and wherein the L-type ligand comprises a cyclic olefin.

14. The invention of claim 13 wherein the cyclic olefin comprises cyclooctadiene.

~~15. The invention of claim 1 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.~~

~~16~~15. The invention of claim ~~15~~ 1 wherein the ruthenium refinery salt further comprises NH_4Cl.

~~17~~16. The invention of claim ~~16~~ 15 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.

~~18~~17. The invention of claim ~~17~~ 16 wherein at least a portion of the NH_4Cl is removed via sublimation.

~~19~~18. The invention of claim ~~18~~ 17 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.

~~20~~19. The invention of claim 1 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of halide ligands, the halide ligands being selected from the group consisting of chloride and bromide.

~~21~~20. The invention of claim 1 wherein the ruthenium intermediate comprises one or a plurality of ammonium cations and one or a plurality of chloride ligands.

~~22~~21. The invention of claim ~~22~~ 20 wherein the ruthenium intermediate further comprises one or a plurality of bromide ligands.

~~23~~22. The invention of claim 1 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$.

~~24~~23. The invention of claim ~~23~~ 22 wherein at least a portion of the $(NH_4)_2RuCl_6$ is crystalline.

~~25~~24. The invention of claim ~~23~~ 22 wherein at least a portion of the $(NH_4)_2RuCl_6$ is a powder.

~~26~~25. The invention of claim 11 wherein the hydrogen chloride is provided in aqueous solution as hydrochloric acid.

~~27~~26. The invention of claim ~~26~~ 25 wherein concentration of the hydrochloric acid is at least about 5 M or higher.

~~28~~27. The invention of claim ~~26~~ 25 wherein concentration of the hydrochloric acid is at least about 6 M or higher.

~~29~~28. The invention of claim 6 wherein the reacting with the hydrogen halide comprises a hydrothermal treatment.

~~30~~29. The invention of claim ~~23~~ 22 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.

~~31~~30. The invention of claim ~~30~~ 29 wherein a reaction temperature in the closed system is at least about 100 °C.

~~32~~31. The invention of claim ~~31~~ 30 wherein at least a portion of the $(NH_4)_2RuCl_6$ is crystalline.

~~33~~32. The invention of claim 6 wherein the reacting with the hydrogen halide comprises atmospheric conditions.

~~34~~33. The invention of claim ~~33~~ 32 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.

~~35~~34. The invention of claim ~~34~~ 33 wherein the ruthenium refinery salt is refluxed in the concentrated hydrochloric acid.

~~36~~35. The invention of claim ~~35~~ 34 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.

~~37~~36. The invention of claim 14 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_6$, and wherein the cyclooctadiene comprises *cis, cis*-1,5-cyclooctadiene.

~~38~~37. The invention of claim 14 wherein the ruthenium intermediate comprises a compound having a structure $(NH_4)_2RuCl_{6l}$ and wherein the reacting of the ruthenium intermediate with cyclooctadiene comprises refluxing the ruthenium intermediate and *cis, cis*-1,5-cyclooctadiene in ethanol.

~~39~~38. The invention of claim 1 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.

~~40~~39. The invention of claim 1 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, such that when two or more of R', R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

~~41~~40. 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 $(NH_4)_2RuCl_5$, $(NH_4)_4[Ru_2OCl_{10}]$, and combinations thereof;
wherein the ruthenium intermediate comprises a compound selected from the group consisting of $(NH_4)_2RuX^16$, $(NH_4)2RuX^1_yX^2_{6-y}$, 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.

~~42~~41. 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.

~~43~~42. The invention of claim ~~42~~41 wherein the converting comprises reacting the

ruthenium carbene complex precursor with a trialkyl phosphine, hydrogen, and a trialkyl amine.

4443. The invention of claim 42-41 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 phosphorous is formed.

4544. The invention of claim 42-41 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.

4645. The invention of claim 45-44 wherein the ruthenium vinylcarbene complex comprises a compound having a structure $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}C(CH_3)_2$.

4746. The invention of claim 43-42 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an N-heterocyclic carbene ligand.

4847. The invention of claim 43-42 further comprising replacing a phosphine ligand of the ruthenium vinylcarbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium vinylcarbene complex.

4948. The invention of claim 48-47 wherein the imidazolidine-containing ruthenium vinylcarbene complex constitutes a second-generation Grubbs-type olefin metathesis catalyst.

5049. The invention of claim 48-47 wherein the imidazolidine ligand comprises 1,3-dimesityl-4,5-dihydroimidazoie.

5150. 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 Cl and Br;

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, such that when two or more of R^1, R^2, and R^3 are taken together, a bidentate ligand to phosphorous is formed.

5251. The invention of claim ~~51~~ 50 wherein the ruthenium carbene complex precursor comprises a structure $RuCl_2(PR^1R^2R^3)_3$.

5352. The invention of claim ~~51~~ 50 wherein each of R^1, R^2, R^3, and R^4 comprises phenyl.

5453. The invention of claim ~~51~~ 50 wherein the converting comprises reacting the ruthenium carbene complex precursor with phenyldiazomethane.

5554. The invention of claim ~~51~~ 50 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.

5655. The invention of claim ~~51~~ 50 further comprising replacing a phosphorous-containing ligand of the ruthenium carbene complex with an imidazolidine ligand to form an imidazolidine-containing ruthenium carbene complex.

5756. A method for preparing a ruthenium complex comprising reacting a ruthenium refinery salt with a hydrogen halide to form the ruthenium complex;

wherein the hydrogen halide comprises hydrogen chloride, hydrogen bromide, or combinations thereof; ~~and~~

wherein the halogen-containing ruthenium complex comprises halogen atoms selected from the group consisting of chlorine and bromine; and

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.

5857. The invention of claim ~~57~~ 56 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 Cl and Br, and wherein y is an integer value from 1 to 6.

~~59~~58. The invention of claim ~~57~~ 56 wherein the ruthenium complex comprises one or a plurality of ammonium cations and one or a plurality of halide ligands, the halide ligands being selected from the group consisting of chloride and bromide.

~~60~~59. The invention of claim ~~57~~ 56 wherein the ruthenium complex comprises one or a plurality of ammonium cations and one or a plurality of chloride ligands.

~~61~~60. The invention of claim ~~57~~ 56 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 Cl and Br; and wherein y is an integer value from 1 to 5.

~~62~~61. The invention of claim ~~57~~ 56 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.

~~63~~62. The invention of claim ~~57~~ 56 wherein the hydrogen halide comprises hydrogen chloride.

~~64~~63. The invention of claim ~~57~~ 56 wherein the hydrogen halide comprises hydrogen bromide.

~~65~~64. The invention of claim ~~57~~ 56 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.

~~66~~65. The invention of claim ~~65~~ 64 wherein the hydrogen chloride is provided in aqueous solution as hydrochloric acid.

~~67~~66. The invention of claim ~~57~~ 56 wherein the reacting with the hydrogen halide comprises a hydrothermal treatment.

~~68~~67. The invention of claim ~~57~~ 56 wherein the reacting with the hydrogen halide comprises atmospheric conditions.

~~69~~68. The invention of claim 1 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, and a combination thereof.

~~70~~69. The invention of claim 1 wherein the L-type ligand comprises a cyclic olefin.

~~71~~70. The invention of claim ~~70~~-69 wherein the cyclic olefin is selected from the group consisting of a diene, a triene, and a combination thereof.

~~72~~71. The invention of claim ~~70~~-69 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.

~~73~~72. The invention of claim ~~70~~-69 wherein the cyclic olefin is selected from the group consisting of cyclooctadiene, cyclododecatriene, and combinations thereof.

~~74~~73. The invention of claim ~~70~~-69 wherein the cyclic olefin comprises 1,5-cyclooctadiene.

~~75~~74. The invention of claim 1 wherein the ruthenium intermediate is a ruthenium (IV) hexahalo complex that comprises a $[RuX^1{}_yX^2{}_{6-y}]^{2-}$ anion, wherein X^1 and X^2 are halogen atoms that are independently selected from the group consisting of Cl and Br; and wherein y is an integer value from 1 to 6.

~~76~~75. The invention of claim ~~75~~-74 wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.

~~77~~76. The invention of claim 1, wherein the ruthenium intermediate is a salt of a ruthenium (IV) hexahalo complex, wherein the halide ligands of the ruthenium (IV) hexahalo complex are selected from the group consisting of chloride and bromide.

~~78~~77. The invention of claim ~~77~~76, wherein the L-type ligand is selected from the group consisting of olefins, phosphines, phosphites, amines, CO, N_2, and combinations thereof.