Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

Figure 2 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

Figure 3 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples. Such discussion is for purposes of illustration only. Modifications to particular examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to one of skill in the art. Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a homogeneous catalyst refers to a catalyst that is present in the same phase (e.g., liquid or gas) as the reactants during catalysis. In contrast, as used herein, a heterogeneous catalyst refers to a catalyst that is in a different phase than the reactants during catalysis.

As used herein, mole percent (mole % or %) and like terms refer to mole percent unless otherwise indicated. Weight percent (wt %) and like terms refer to weight percent unless otherwise indicated.

"Conversion" refers to the fraction of reactant consumed in the reaction and is expressed as a mass percentage based on the amount of carboxylic acid in

fractionated and collected in a collection flask **30**. The condensers **40, 50** serve to recover an optimal amount of product and solvent while releasing non-condensible gases. The temperature of the condensers **40, 50** is regulated by conventional means known to one of skill in the art. The order of addition of the reactants is not crucial in the process of this invention.

Examples

The following examples are presented to further illustrate the present invention and should not be taken as limiting the invention, the spirit and scope of which is set forth in the appended claims. These examples are provided for illustrative purposes only and various modifications thereof can readily be made which are known to one skilled in the art.

Examples 1-23 illustrate the conversion of benzoic acid to vinyl benzoate using various catalysts of this invention. The selectivity to vinyl benzoate and TONs achieved by Examples 1 and 3-23 are displayed in summary form in **Figures 2** and **3**, respectively.

Specifically, Examples 1-6 illustrate the catalytic activity of various platinum metal complexes with or without ligands and/or additives. Examples 7-11 illustrate the catalytic activity of various rhenium metal complexes with or without ligands and/or additives. Examples 12 and 13 illustrate the catalytic activity of various rhodium metal complexes with or without ligands and/or additives. Examples 14-17 illustrate the catalytic activity of various ruthenium metal complexes with or without ligands and/or additives. Examples 18-20 illustrate the catalytic activity of various palladium metal complexes with or without ligands and/or additives. Examples 21-23 illustrate the catalytic activity of various iridium metal complexes with or without ligands and/or additives.

Examples 24-33 illustrate the conversion of 2-ethylhexanoic acid to vinyl 2-ethylhexanoate using various catalysts of this invention. Examples 34-43

additives were also used at a metal/ligand molar ratio of one. The results showed that the best performance of zinc catalyst system showed a TON of less than 0.5.

Comparative Example 4

Example 1 was substantially repeated except for using zinc acetylacetonate in combination with cadmium acetylacetonate as an additive. The reaction was run at 180°C in butyl benzoate as the solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and 50 milligrams of the catalyst. The TON of ~0.51 was obtained. No improvement was observed with any of the ligands and/or additives tested.

Comparative Example 5

Example 1 was substantially repeated except for using zinc acetylacetonate as the catalyst. The reaction was run at 180°C in butyl benzoate as the solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and 50 milligrams of the catalyst. The TON of ~0.45 was obtained.

While the invention has been described in connection with several embodiments, modifications of those embodiments within the spirit and scope of the present invention will be readily apparent to those of skill in the art. The invention is defined in the appended claims.

WHAT IS CLAIMED IS:

1. A homogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a homogeneous catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives or a mixture thereof; wherein the catalyst is a metal complex, said metal is selected from the group consisting of iridium, palladium, platinum, rhenium, rhodium and ruthenium; and wherein the catalyst and optionally the ligand(s) and additive(s) are selected and utilized in amounts such that selectivity to the vinyl ester is at least 50%.

2. The process according to Claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50% and a Relative Activity of at least 80.

3. The process according to Claim 1, wherein said carboxylic acid is selected from the group consisting of benzoic acid, 2-ethyl hexanoic acid, neopentanoic acid, neoheptanoic acid and neodecanoic acid.

4. The process according to Claim 1, wherein the metal of the homogeneous catalyst is complexed with at least one compound or radical selected from the group consisting of fluoride, chloride, iodide, acetate, acetylacetonate, dimethyl, carbonyl, 1,5-cyclooctadiene, methoxy, 5-indenyl, tetrafluoroborate, [1,3-bis(diphenylphosphino)propane]-bis(benzonitrile), bromopentacarbonyl, butane, triphenylphosphine, and bis(2-methylallyl).

5. The process according to Claim 1, wherein an initial reaction mixture comprises a mixture of said metal complex catalyst and benzoic acid in a molar acid:metal ratio of from about 100:1 to about 5000:1.

6. The process according to Claim 1, wherein the reaction temperature ranges from about 25°C to about 250°C.

7. The process according to Claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

8. The process according to Claim 1, wherein the solvent is selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

9. The process according to Claim 1, wherein said ligand is selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), from (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; and said additive is selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

10. A homogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in a suitable organic solvent, with acetylene in the presence of a homogeneous catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands or additives thereof; wherein the catalyst is a

metal complex, said metal selected from the group consisting of platinum, rhenium, rhodium, ruthenium, and palladium, and wherein the catalyst and optionally the ligand(s) and additive(s) are selected and utilized in amounts such that the Relative Activity is at least 100.

11. The process according to Claim 10, wherein said carboxylic acid is benzoic acid.

12. The process according to Claim 10, wherein said carboxylic acid is 2-ethylhexanoic acid.

13. The process according to Claim 10, wherein the carboxylic acid and catalyst are provided in a molar acid:metal ratio of from about 180:1 to about 3000:1.

14. The process according to Claim 10, wherein the reaction temperature ranges from about 50°C to about 180°C.

15. The process according to Claim 10, wherein the catalyst exhibits a Relative Activity (moles of vinyl ester/metal atom) of about 100 to about 1000.

16. The process according to Claim 10, wherein the selectivity to vinyl ester based on carboxylic acid consumed is at least 60 percent.

17. A homogeneous process for the selective formation of vinyl 2-ethylhexanoate from 2-ethylhexanoic acid which comprises reacting 2-ethylhexanoic acid with acetylene optionally in a suitable organic solvent, at a suitable reaction temperature and pressure in the presence of a homogeneous catalyst and optionally in the presence of one or more ligands or additives thereof; wherein the catalyst is a metal complex, said metal selected from the group consisting of platinum, rhenium, rhodium, ruthenium, and palladium, and wherein the the

2-ethylhexanoic acid is provided in a molar ratio of 2-ethylhexanoic acid:catalyst metal of about 200:1 to about 4000:1.

18. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a palladium catalyst and optionally in the presence of 1,2-diphenylphosphino benzene (1,2-DPPB) as a ligand, wherein the catalyst is palladium (II) acetate and the carboxylic acid is provided in a molar ratio of carboxylic acid:palladium metal of about 200:1 to about 4000:1.

19. The process according to Claim 18, wherein the reaction temperature ranges from about 150°C to about 170°C.

20. The process according to Claim 18, wherein the ligand is present in a ligand:metal molar ratio of about 0.5:1 to about 1:1.

21. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a ruthenium catalyst and optionally in the presence of 1,2-diphenylphosphino benzene (1,2-DPPB) or triphenylphosphine as a ligand, wherein the catalyst is selected from bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium (II) and triruthenium dodecacarbonyl and the carboxylic acid is provided in a molar ratio of carboxylic acid:ruthenium metal of about 200:1 to about 4000:1.

22. The process of Claim 21, wherein the catalyst is triruthenium dodecacarbonyl, benzoic acid is provided in a benzoic acid:metal ratio of from 200:1 to about 400:1, the reaction temperature is about 150°C to about 170°C, and a ligand is present in a ligand:metal molar ratio of from about 0.5:1 to about 1:1.

23. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a rhodium catalyst and optionally in the presence of a ligand selected from the group consisting of 1,2-diphenylphosphino benzene (1,2-DPPB), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), diphenyl-2-pyridylphosphine and triphenylphosphine, wherein the catalyst is selected from [1,4-bis(diphenyl-phosphino)butane](1,5-cyclooctadiene)rhodium (I) tetrafluoroborate, tetrarhodium dodecacarbonyl or rhodium (II) acetate dimer and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhodium metal of about 200:1 to about 500:1.

24. The process according to Claim 23, wherein the reaction temperature is from about 110°C to about 170°C.

25. The process according to Claim 23, wherein the ligand is present in a ligand:metal molar ratio of from about 0.5 to about 1.5.

26. The process according to Claim 23, wherein the catalyst is tetrarhodium dodecacarbonyl and the ligand is oxydi-(2,1-phenylene)bis(diphenylphosphine) or diphenyl-2-pyridylphosphine.

27. The process according to Claim 23, wherein the catalyst is rhodium(II)acetate dimer, and the ligand is selected from the group consisting of oxydi-(2,1-phenylene)bis(diphenylphosphine), triphenylphosphine, and 1,2-diphenylphosphinobenzene.

28. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in

a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a platinum catalyst and optionally in the presence of a ligand selected from the group consisting of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), and triphenylphosphine, wherein the catalyst is selected from platinum acetylacetonate, platinum iodide or (1,5-cyclooctadiene)dimethylplatinum(II) and the carboxylic acid is provided in a molar ratio of carboxylic acid:platinum metal of about 200:1 to about 5000:1.

29. The process according to claim 28, wherein the reaction temperature is in the range of about 130°C to about 170°C.

30. The process according to Claim 28, wherein the metal complex catalyst is platinum acetylacetonate and the reaction temperature is from about 140° to about 160°C.

31. The process according to Claim 30, wherein the ligand is 4,5-bis(diphenyl-phosphino)-9,9-dimethylxanthene in a ligand:metal molar ratio of from 0.5:1 to 2:1.

32. The process according to Claim 28, wherein the metal complex catalyst is (1,5-cyclooctadiene)dimethylplatinum (II) and the reaction temperature is from about 140° to about 160°C.

33. The process according to Claim 32, wherein the ligand is 4,5-bis(diphenyl-phosphino)-9,9-dimethylxanthene in a ligand:metal molar ratio of from 0.4:1 to 2:1.

34. The process according to Claim 28, wherein the metal catalyst is platinum iodide and the temperature is about 140°C.

35. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a rhenium catalyst and optionally in the presence of a ligand chosen from (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)ferrocene, 1,2-diphenylphosphinobenzene, 1,2-bis(diphenylphosphino)benzene, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), triphenylphosphine, tris(4-methoxyphenyl)phosphine, and tris(p-trifluoromethylphenyl)phosphine, and optionally including as an additive potassium acetate or sodium benzoate, wherein the catalyst is selected from pentacarbonylchlororhenium (I), dirhenium decacarbonyl, or bromopentacarbonylrhenium (I), and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhenium metal of about 150:1 to about 1500:1.

36. The process according to Claim 35, wherein the reaction temperature is in the range of about 110°C to about 170°C.

37. The process according to Claim 35, wherein the ligand is present in a ligand:metal molar ratio of from about 0.4 to about 1.5:1.

38. The process according to Claim 35, wherein the metal catalyst is bromopentacarbonylrhenium (I), optionally the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-2,1-phenylenebis(diphenylphosphine), or 1,2-diphenylphosphinobenzene, and optionally the additive is potassium acetate.

39. The process according to Claim 35, wherein the metal complex catalyst is dirhenium decacarbonyl and optionally the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), or tris(4-methoxyphenyl)phosphine.

40. The process according to Claim 35, wherein the metal catalyst is pentacarbonylchlororhenium (I), optionally the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, 1,2-bis(diphenylphosphino)benzene, or oxydi-(2,1-phenylene)bis(diphenylphosphine) and optionally the additive is sodium benzoate.

41. A homogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a platinum catalyst and optionally in the presence of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene as a ligand, wherein the catalyst is selected from platinum acetylacetonate or (1,5-cyclooctadiene)dimethylplatinum(II) and the benzoic acid is provided in a molar ratio of benzoic acid:platinum metal of about 250:1 to about 5000:1.

42. A homogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a rhenium catalyst and optionally in the presence of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene as a ligand, wherein the catalyst is selected from pentacarbonylchlororhenium (I), dirhenium decacarbonyl, or bromopentacarbonylrhenium (I), and the benzoic acid is provided in a molar ratio of benzoic acid:rhenium metal of about 150:1 to about 1500:1.

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WHAT IS CLAIMED IS:

1. A homogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid optionally dissolved in a suitable organic solvent with acetylene in the presence of a homogeneous catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine,1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, or optionally in the presence of one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate, or a mixture thereof; wherein the catalyst is a metal complex, said metal is selected from the group consisting of iridium, palladium, platinum, and rhodium; and wherein reaction temperature and pressure, the catalyst and optionally the ligand(s) and additive(s) are selected such that selectivity to the vinyl ester is at least 50%; and wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic, neoheptanoic, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

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2. The process according to Claim 1, wherein the process is further characterized by a carboxylic acid conversion of at least 50% and a Relative Activity of at least 80.

3. The process according to Claim 1, wherein said carboxylic acid is selected from the group consisting of benzoic acid, 2-ethyl hexanoic acid, neopentanoic acid, neoheptanoic acid and neodecanoic acid.

4. The process according to Claim 1, wherein the metal of the homogeneous catalyst is complexed with at least one compound or radical selected from the group consisting of fluoride, chloride, iodide, acetate, acetylacetonate, dimethyl, carbonyl, 1,5-cyclooctadiene, methoxy, 5-indenyl, tetrafluoroborate, [1,3-bis(diphenylphosphino)propane]-bis(benzonitrile), bromopentacarbonyl, butane, triphenylphosphine, and bis(2-methylallyl).

5. The process according to Claim 1, wherein an initial reaction mixture comprises a mixture of said metal complex catalyst and benzoic acid in a molar acid:metal ratio of from about 100:1 to about 5000:1.

6. The process according to Claim 1, wherein the reaction temperature ranges from about 25°C to about 250°C.

7. The process according to Claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

8. The process according to Claim 1, wherein the solvent is selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

9. The process according to Claim 1, wherein said ligand is selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-

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DPPB), oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; and optionally one or more additives are selected from the group consisting of potassium acetate, sodium benzoate, and sodium tetrafluoroborate.

10. A homogeneous process for selective formation of a vinyl ester from a carboxylic acid comprising: reacting a carboxylic acid, optionally dissolved in a suitable organic solvent, with acetylene in the presence of a homogeneous catalyst at a suitable reaction temperature and pressure, and optionally in the presence of one or more ligands selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, or additives selected from the group consisting of potassium acetate, sodium benzoate, sodium tetrafluoroborate, or a mixture thereof; wherein the catalyst is a metal complex, said metal selected from the group consisting of platinum, rhodium, and palladium, and wherein reaction temperature and pressure, the catalyst and optionally the ligand(s) and additive(s) are selected such that the Relative Activity is at least 100.

11. The process according to Claim 10, wherein said carboxylic acid is benzoic acid.

12. The process according to Claim 10, wherein said carboxylic acid is 2-ethylhexanoic acid.

13. The process according to Claim 10, wherein the carboxylic acid and catalyst are provided in a molar acid:metal ratio of from about 180:1 to about 3000:1.

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14. The process according to Claim 10, wherein the reaction temperature ranges from about 50°C to about 180°C.

15. The process according to Claim 10, wherein the catalyst exhibits a Relative Activity (moles of vinyl ester/metal atom) of about 100 to about 1000.

16. The process according to Claim 10, wherein the selectivity to vinyl ester based on carboxylic acid consumed is at least 60 percent.

17. A homogeneous process for the selective formation of vinyl 2-ethylhexanoate from 2-ethylhexanoic acid which comprises reacting 2-ethylhexanoic acid with acetylene optionally in a suitable organic solvent, at a suitable reaction temperature and pressure in the presence of a homogeneous catalyst and optionally in the presence of one or more ligands selected from the group consisting of triphenylphosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, or additives selected from the group consisting of potassium acetate, sodium benzoate, sodium tetrafluoroborate, or a mixture thereof; wherein the catalyst is a metal complex, said metal selected from the group consisting of platinum, rhodium, and palladium, and wherein the 2-ethylhexanoic acid is provided in a molar ratio of 2-ethylhexanoic acid:catalyst metal of about 200:1 to about 4000:1.

18. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a palladium catalyst and optionally in the presence of 1,2-diphenylphosphino benzene (1,2-DPPB) as a ligand, wherein the catalyst is

palladium (II) acetate and the carboxylic acid is provided in a molar ratio of carboxylic acid:palladium metal of about 200:1 to about 4000:1.

19. The process according to Claim 18, wherein the reaction temperature ranges from about 150°C to about 170°C.

20. The process according to Claim 18, wherein the ligand is present in a ligand:metal molar ratio of about 0.5:1 to about 1:1.

21. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid selected from the group consisting of benzoic acid, neopentanoic, neoheptanoic, neodecanoic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a ruthenium catalyst and optionally in the presence of 1,2-diphenylphosphino benzene (1,2-DPPB) or triphenylphosphine as a ligand, wherein the catalyst is selected from bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium (II) and triruthenium dodecacarbonyl and the carboxylic acid is provided in a molar ratio of carboxylic acid:ruthenium metal of about 200:1 to about 4000:1.

22. The process of Claim 21, wherein the catalyst is triruthenium dodecacarbonyl, the carboxylic acid is benzoic acid ~~is~~ provided in a benzoic acid:metal ratio of from 200:1 to about 400:1, the reaction temperature is about 150°C to about 170°C, and a ligand is present in a ligand:metal molar ratio of from about 0.5:1 to about 1:1.

23. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a rhodium catalyst and optionally in the presence of a ligand

selected from the group consisting of 1,2-diphenylphosphino benzene (1,2-DPPB), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), diphenyl-2-pyridylphosphine and triphenylphosphine, wherein the catalyst is selected from [1,4-bis(diphenyl-phosphino)butane](1,5-cyclooctadiene)rhodium (I) tetrafluoroborate, tetrarhodium dodecacarbonyl or rhodium (II) acetate dimer and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhodium metal of about 200:1 to about 500:1.

24. The process according to Claim 23, wherein the reaction temperature is from about 110°C to about 170°C.

25. The process according to Claim 23, wherein the ligand is present in a ligand:metal molar ratio of from about 0.5 to about 1.5.

26. The process according to Claim 23, wherein the catalyst is tetrarhodium dodecacarbonyl and the ligand is oxydi-(2,1-phenylene)bis(diphenylphosphine) or diphenyl-2-pyridylphosphine.

27. The process according to Claim 23, wherein the catalyst is rhodium(II)acetate dimer, and the ligand is selected from the group consisting of oxydi-(2,1-phenylene)bis(diphenylphosphine), triphenylphosphine, and 1,2-diphenylphosphinobenzene.

28. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a platinum catalyst and optionally in the presence of a ligand selected from the group consisting of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, oxydi-(2,1-phenylene)bis(diphenylphosphine), and triphenylphosphine, wherein the catalyst is selected from platinum

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acetylacetonate, platinum iodide or (1,5-cyclooctadiene)dimethylplatinum(II) and the carboxylic acid is provided in a molar ratio of carboxylic acid:platinum metal of about 200:1 to about 5000:1.

29. The process according to claim 28, wherein the reaction temperature is in the range of about 130°C to about 170°C.

30. The process according to Claim 28, wherein the metal complex catalyst is platinum acetylacetonate and the reaction temperature is from about 140° to about 160°C.

31. The process according to Claim 30, wherein the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene in a ligand:metal molar ratio of from 0.5:1 to 2:1.

32. The process according to Claim 28, wherein the metal complex catalyst is (1,5-cyclooctadiene)dimethylplatinum (II) and the reaction temperature is from about 140° to about 160°C.

33. The process according to Claim 32, wherein the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene in a ligand:metal molar ratio of from 0.4:1 to 2:1.

34. The process according to Claim 28, wherein the metal catalyst is platinum iodide and the temperature is about 140°C.

35. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid selected from the group consisting of benzoic acid, neopentanoic, neoheptanoic, neodecanoic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid which comprises reacting the carboxylic acid with acetylene in a suitable organic

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solvent at a suitable reaction temperature and pressure in the presence of a rhenium catalyst and a ligand chosen from the group consisting of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene and oxydi-(2,1-phenylene)bis(diphenylphosphine), and optionally including as an additive potassium acetate or sodium benzoate, wherein the catalyst is selected from pentacarbonylchlororhenium (I), dirhenium decacarbonyl, or bromopentacarbonylrhenium (I), and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhenium metal of about 150:1 to about 1500:1.

36. The process according to Claim 35, wherein the reaction temperature is in the range of about 110°C to about 170°C.

37. The process according to Claim 35, wherein the ligand is present in a ligand:metal molar ratio of from about 0.4 to about 1.5:1.

38. The process according to Claim 35, wherein the metal catalyst is bromopentacarbonylrhenium (I), and optionally the additive is potassium acetate.

39. The process according to Claim 35, wherein the metal complex catalyst is dirhenium decacarbonyl and the ligand is 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

40. The process according to Claim 35, wherein the metal catalyst is pentacarbonylchlororhenium (I) and optionally the additive is sodium benzoate.

41. A homogeneous process for the selective formation of vinyl benzoate from benzoic acid which comprises reacting benzoic acid with acetylene in a suitable organic solvent at a suitable reaction temperature and pressure in the presence of a platinum catalyst and optionally in the presence of 4,5-

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bis(diphenylphosphino)-9,9-dimethylxanthene as a ligand, wherein the catalyst is selected from platinum acetylacetonate or (1,5-cyclooctadiene)dimethyl-platinum(II) and the benzoic acid is provided in a molar ratio of benzoic acid:platinum metal of about 250:1 to about 5000:1.

42. The homogeneous process according to Claim 41, wherein the platinum catalyst exhibits a Relative Activity of at least 400.

43. The homogeneous process according to Claim 41, wherein the platinum catalyst exhibits a Relative Activity of at least 500.

44. The homogeneous process according to Claim 41, wherein the platinum catalyst exhibits a Relative Activity of at least 600.

45. The homogeneous process according to Claim 41, wherein the platinum catalyst exhibits a Relative Activity in the range of from about 450 to about 650.

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WHAT IS CLAIMED IS:

1. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and suitable pressure for 1-5 hours in the presence of a metal complex catalyst and optionally in the presence of a ligand, wherein the metal is selected from the group consisting of Rh, Pd, Re, Ir and Pt, provided in a molar ratio of carboxylic acid: metal of 200:1 to 4000:1.

2. The process according to claim 1, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

3. The process according to claim 1, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

4. The process of claim 1, wherein the reaction temperature ranges from 40°C to 150°C.

5. The process according to claim 1, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

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6. The process according to claim 1, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

7. The process according to claim 1, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminium chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, tririutheniumdodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

8. The process according to claim 1, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

9. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from platinum acetylacetonate, (1,5-cyclooctadiene)dimethylplatinum (II), platinum (II) chloride, platinum (IV) chloride, platinum (II) bromide, platinum (II) iodide, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disoloxane and *cis*-bis(benzonitrile)-dichloroplatinum(II), and the carboxylic acid is provided in a molar ratio of carboxylic acid:platinum metal of 200:1 to 4000:1.

10. The process according to claim 9, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid,

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neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

11. The process according to claim 9, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

12. The process of claim 9, wherein the reaction temperature ranges from 80°C to 180°C.

13. The process according to claim 9, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

14. The process according to claim 9, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

15. The process according to claim 9, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, tririutheniumdodecacarbonyl

($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

16. The process according to claim 9, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

17. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from (1,5-cyclooctadiene)-hexafluoroacetylacetonato)iridium(I), iridium (III) acetylacetonate, bis(1,5-cyclooctadiene)diiridium(I) dichloride, (acetylacetonato)(1,5-cyclooctadiene)iridium(I), (1,5-cyclooctadiene)(methoxy)iridium(I) dimer, (1,5-cyclooctadiene)-5-indenyliridium(I), and bis(1,5-cyclooctadiene)iridium(I) tetrafluoroborate, and the carboxylic acid is provided in a molar ratio of carboxylic acid:iridium metal of 200:1 to 4000:1.

18. The process according to claim 17, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

19. The process according to claim 17, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-

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phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

20. The process of claim 17, wherein the reaction temperature ranges from 40°C to 180°C.

21. The process according to claim 17, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

22. The process according to claim 17, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

23. The process according to claim 17, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

24. The process according to claim 17, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

25. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene,

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optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from [1,4-bis(diphenylphosphino)butane](1,5-cyclooctadiene)rhodium (I) tetrafluoroborate, tetrarhodium dodecacarbonyl, (acetylacetonato)dicarbonylrhodium(I), 1,1'-bis(diisopropylphosphino)ferrocene(cod)Rh-phosphotungstic acid, *bis*(1,5-dicyclooctadiene)dirhodium(I)dichloride, tetrarhodium dodecacarbonyl, dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer, methoxy(cyclooctadiene)rhodium(I) dimer, or rhodium (II) acetate dimer, and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhodium metal of 200:1 to 4000:1.

26. The process according to claim 25, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

27. The process according to claim 25, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine,1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

28. The process of claim 25, wherein the reaction temperature ranges from 50°C to 180°C.

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29. The process according to claim 25, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

30. The process according to claim 25, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

31. The process according to claim 25, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

32. The process according to claim 25, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

33. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and suitable pressure for 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is palladium (II) acetate or palladium (II)[1,3-*bis*(diphenylphosphino)propane]-*bis*(benzonitrile)-*bis*-tetrafluoroborate, and the carboxylic acid is provided in a molar ratio of carboxylic acid:palladium metal of 200:1 to 4000:1.

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34. The process according to claim 33, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

35. The process according to claim 33, wherein the ligand is present and selected from the group consisting of tris(1-naphthyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

36. The process of claim 33, wherein the reaction temperature ranges from 60°C to 180°C.

37. The process according to claim 33, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

38. The process according to claim 33, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

39. The process according to claim 33, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, tririutheniumdodecacarbonyl

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($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

40. The process according to claim 33, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

41. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from Bromopentacarbonylrhenium(I), Dirhenium decacarbonyl, or Pentacarbonylchlororhenium(I), and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhenium metal of 200:1 to 4000:1.

42. The process according to claim 41, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

43. The process according to claim 41, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

44. The process of claim 41, wherein the reaction temperature ranges from 80°C to 180°C.

45. The process according to claim 41, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

46. The process according to claim 41, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

47. The process according to claim 41, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, tririutheniumdodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

48. The process according to claim 41, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

49. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and suitable pressure in the presence of a metal complex catalyst and optionally in the presence of a ligand, wherein the metal is selected from the

group consisting of Rh, Pd, Re, Ir and Pt, provided in a molar ratio of carboxylic acid: metal of 200:1 to 4000:1.

50. The process according to claim 49, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

51. The process according to claim 49, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine,1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

52. The process of claim 49, wherein the reaction temperature ranges from 40°C to 180°C.

53. The process according to claim 49, wherein the pressure of the reaction mixture is from 101.325 kilopascals to 202.650 kilopascals.

54. The process according to claim 49, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

55. The process according to claim 49, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride,

cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

56. The process according to claim 49, wherein said ligand is present in a ligand: metal molar ratio of 0.5:1 to 1.5:1.

Figure 1 is a schematic diagram of an apparatus suitable for producing vinyl ester from a carboxylic acid and acetylene in accordance with the process of the present invention;

Figure 2 is an illustration of the relative selectivity to vinyl benzoate achieved using a variety of catalyst metals according to the process of the invention; and

Figure 3 is an illustration of the Relative Activity achieved using a variety of catalyst metals according to the process of the invention.

Detailed Description of the Invention

The invention is described in detail below with reference to several embodiments and numerous examples.

Terminology used herein is given its ordinary meaning consistent with the exemplary definitions set forth immediately below.

As used herein, a homogeneous catalyst refers to a catalyst that is present in the same phase (e.g., liquid or gas) as the reactants during catalysis. In contrast, as used herein, a heterogeneous catalyst refers to a catalyst that is in a different phase than the reactants during catalysis.

As used herein, mole percent (mole % or %) and like terms refer to mole percent unless otherwise indicated. Weight percent (wt %) and like terms refer to weight percent unless otherwise indicated.

"Conversion" refers to the fraction of reactant consumed in the reaction and is expressed as a mass percentage based on the amount of carboxylic acid in

fractionated and collected in a collection flask **30**. The condensers **40, 50** serve to recover an optimal amount of product and solvent while releasing non-condensible gases. The temperature of the condensers **40, 50** is regulated by conventional means known to one of skill in the art. The order of addition of the reactants is not crucial in the process of this invention.

Examples

The following examples are presented to further illustrate the present invention.

Examples 1-23 illustrate the conversion of benzoic acid to vinyl benzoate using various catalysts of this invention. The selectivity to vinyl benzoate and TONs achieved by Examples 1 and 3-23 are displayed in summary form in **Figures 2** and **3**, respectively.

Specifically, Examples 1-6 illustrate the catalytic activity of various platinum metal complexes with or without ligands and/or additives. Examples 7-11 illustrate the catalytic activity of various rhenium metal complexes with or without ligands and/or additives. Examples 12 and 13 illustrate the catalytic activity of various rhodium metal complexes with or without ligands and/or additives. Examples 14-17 illustrate the catalytic activity of various ruthenium metal complexes with or without ligands and/or additives. Examples 18-20 illustrate the catalytic activity of various palladium metal complexes with or without ligands and/or additives. Examples 21-23 illustrate the catalytic activity of various iridium metal complexes with or without ligands and/or additives.

Examples 24-33 illustrate the conversion of 2-ethylhexanoic acid to vinyl 2-ethylhexanoate using various catalysts of this invention. Examples 34-43

additives were also used at a metal/ligand molar ratio of one. The results showed that the best performance of zinc catalyst system showed a TON of less than 0.5.

Comparative Example 4

Example 1 was substantially repeated except for using zinc acetylacetonate in combination with cadmium acetylacetonate as an additive. The reaction was run at 180°C in butyl benzoate as the solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and 50 milligrams of the catalyst. The TON of ~0.51 was obtained. No improvement was observed with any of the ligands and/or additives tested.

Comparative Example 5

Example 1 was substantially repeated except for using zinc acetylacetonate as the catalyst. The reaction was run at 180°C in butyl benzoate as the solvent. The amount of benzoic acid used was 100 milligrams in combination with 500 ppm of para-benzoquinone and 50 milligrams of the catalyst. The TON of ~0.45 was obtained.

The invention is defined in the appended claims.

What is claimed is:

1. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for about 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from platinum acetylacetonate, (1,5-cyclooctadiene) dimethylplatinum(II), platinum(II)chloride, platinum(IV) chloride, platinum(II)bromide, platinum(II)iodide, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl-disoloxane and cis-bis (benzonitrile)-dichloroplatinum(II), and the carboxylic acid is provided in a molar ratio of carboxylic acid:platinum metal of about 200:1 to about 4000:1.

2. The process according to claim 1, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

3. The process according to claim 1, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

4. The process of claim 1, wherein the reaction temperature ranges from about 80° C. to about 180° C.

5. The process according to claim 1, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

6. The process according to claim 1, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

7. The process according to claim 1, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, trirutheniumdodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

8. The process according to claim 1, wherein said ligand is present in a ligand:metal molar ratio of about 0.5:1 to about 1.5:1.

9. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for about 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from (1,5-cyclooctadiene)-hexafluoroacetylacetonato)iridium(I), iridium(III)acetylacetonate, bis(1,5-cyclooctadiene)diiridium(I)dichloride, (acetylacetonato)(1,5-cyclooctadiene)iridium(I), (1,5-cyclooctadiene)(methoxy) iridium(I)dimer, (1,5-cyclooctadiene)-5-indenyliridium(I), and bis(1,5-cyclooctadiene)iridium(I)tetrafluoroborate, and the carboxylic acid is provided in a molar ratio of carboxylic acid:iridium metal of about 200:1 to about 4000:1.

10. The process according to claim 9, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

11. The process according to claim 9, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-

ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

12. The process of claim 9, wherein the reaction temperature ranges from about 40° C. to about 180° C.

13. The process according to claim 9, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

14. The process according to claim 9, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

15. The process according to claim 9, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

16. The process according to claim 9, wherein said ligand is present in a ligand:metal molar ratio of about 0.5:1 to about 1.5:1.

17. A homogeneous process for the selective formation of a vinyl ester from a carboxylic acid which comprises reacting the carboxylic acid with acetylene, optionally in a suitable organic solvent, at a suitable reaction temperature and pressure for about 1-5 hours in the presence of a catalyst and optionally in the presence of a ligand, wherein the catalyst is selected from [1,4-bis(diphenyl-phosphino)butane](1,5-cyclooctadiene)rhodium(I)tetrafluoroborate, tetrarhodium dodecacarbonyl, (acetylacetonato)dicarbonylrhodium(I), 1,1'-bis(diisopropylphosphino)ferrocene(cod)Rh-phosphotungstic acid, bis(1,5-dicyclooctadiene)dirhodium(I)dichloride, tetrarhodium dodecacarbonyl, dichloro(pentamethylcyclopentadienyl)rhodium(III)dimer, methoxy(cylooctadiene) rhodium(I)dimer, or rhodium(II)acetate dimer, and the carboxylic acid is provided in a molar ratio of carboxylic acid:rhodium metal of about 200:1 to about 4000:1.

18. The process according to claim 17, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neopentanoic acid, neoheptanoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, and stearic acid.

19. The process according to claim 17, wherein the ligand is present and selected from the group consisting of triphenylphosphine, tris(4-methoxyphenyl)-phosphine, tris(p-trifluoromethylphenyl)-phosphine, tris(1-naphthyl)phosphine, tris(2,4,6-trimethoxyphenyl)phosphine, 1,2-diphenylphosphinobenzene (1,2-DPPB), o-bipyridyl, oxydi-(2,1-phenylene)bis(diphenylphosphine), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, 1,1'-bis(diphenylphosphino)-ferrocene, 1,2-bis(diphenylphosphino)benzene, diphenyl-2-pyridylphosphine and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

20. The process of claim 17, wherein the reaction temperature ranges from about 50° C. to about 180° C.

21. The process according to claim 17, wherein the pressure of the reaction mixture is from about one atmosphere to two atmospheres absolute.

22. The process according to claim 17, wherein the solvent is present and selected from the group consisting of acetonitrile, benzonitrile, butyl benzoate, mineral oil, diethylene glycol dibutylether and toluene.

23. The process according to claim 17, utilizing one or more additives selected from the group consisting of aluminum acetylacetonate, aluminum chloride, cadmium acetylacetonate, cerium chloride, iron chloride, potassium acetate, lithium acetate, lithium bromide, lithium chloride, sodium benzoate, sodium phosphate, sodium tetrafluoroborate, sodium chloride, sodium iodide, sodium trifluoroacetate, para-benzoquinone, palladium acetate, palladium acetylacetonate, palladium chloride, triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$), zinc bromide, zinc chloride, benzoic anhydride, tri-(n-butyl)amine, tetra-(n-butyl)ammonium chloride, sodium phosphate and tetrabutylammonium acetate.

24. The process according to claim 17, wherein said ligand is present in a ligand:metal molar ratio of about 0.5:1 to about 1.5:1.