

METHOD AND CATALYST SYSTEM FOR PRODUCING AROMATIC CARBONATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to a method and catalyst system for producing aromatic carbonates and, more specifically, to a method and catalyst system for producing diaryl carbonates through the carbonylation of aromatic hydroxy compounds.

2. Discussion of Related Art:

Aromatic carbonates find utility, *inter alia*, as intermediates in the preparation of polycarbonates. For example, a popular method of polycarbonate preparation is the melt transesterification of aromatic carbonates with bisphenols. This method has been shown to be environmentally superior to previously used methods which employed phosgene, a toxic gas, as a reagent and chlorinated aliphatic hydrocarbons, such as methylene chloride, as solvents.

Various methods for preparing aromatic carbonates have been previously described in the literature and/or utilized by industry. A method that has enjoyed substantial popularity in the literature involves the direct carbonylation of aromatic hydroxy compounds with carbon monoxide and oxygen. In general, practitioners have found that the carbonylation reaction requires a rather complex catalyst system. For example, in U.S. Patent No. 4,187,242, which is assigned to the assignee of the present invention, Chalk reports that a carbonylation catalyst system should contain a Group VIII B metal, such as ruthenium, rhodium, palladium, osmium, iridium,

platinum, or a complex thereof. Further refinements to the carbonylation reaction include the identification of organic co-catalysts, such as terpyridines, phenanthrolines, quinolines and isoquinolines in U.S. Patent No. 5,284,964 and the use of certain halide compounds, such as quaternary ammonium or phosphonium halides in U.S. Patent No. 5,399,734, both patents also being assigned to the assignee of the present invention.

The economics of the carbonylation process is strongly dependent on the number of moles of aromatic carbonate produced per mole of Group VIII B metal utilized (i.e. "catalyst turnover"). Consequently, much work has been directed to the identification of efficacious inorganic co-catalysts that increase catalyst turnover. In U.S. Patent No. 5,231,210, which is also assigned to General Electric Company, Joyce et al. report the use of a cobalt pentadentate complex as an inorganic co-catalyst ("IOCC"). In U.S. Patent No. 5,498,789, Takagi et al. report the use of lead as an IOCC. In U.S. Patent No. 5,543,547, Iwane et al. report the use of trivalent cerium as an IOCC. In U.S. Patent No. 5,726,340, Takagi et al. report the use of lead and cobalt as a binary IOCC system. In Japanese Unexamined Patent Application No. 10-316627, Yoneyama et al. report the use of manganese and the combination of manganese and lead as IOCC's.

The literature is silent, however, as to the role of the IOCC in the carbonylation reaction (i.e. the reaction mechanism). Accordingly, meaningful guidance regarding the identification of additional IOCC systems is cursory at best. Periodic table groupings have failed to provide guidance in identifying additional IOCC's. For example, U.S. Patent No. 5,856,554 provides a general listing of possible IOCC candidates, yet further analysis has revealed that many of the members (and combinations of members) of the recited groups (i.e., Groups IV B and V B) do not catalyze the carbonylation reaction. Therefore, due to the lack of guidance in the literature, the identification of effective carbonylation catalyst systems has become a serendipitous exercise.

As the demand for high performance plastics has continued to grow, new and improved methods of providing product more economically are needed to supply the market. In this context, various processes and catalyst systems are constantly being evaluated; however, the identities of improved and/or additional effective catalyst systems for these processes continue to elude the industry. Consequently, a long felt, yet unsatisfied need exists for new and improved methods and catalyst systems for producing aromatic carbonates and the like.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a method and catalyst system for producing aromatic carbonates. In one embodiment, the present invention provides a method of carbonylating aromatic hydroxy compounds by contacting at least one aromatic hydroxy compound with oxygen and carbon monoxide in the presence of a carbonylation catalyst system that includes a catalytic amount of an inorganic co-catalyst containing lead and a catalytic amount of an inorganic co-catalyst containing titanium.

In various alternative embodiments, the carbonylation catalyst system can include an effective amount of a palladium source and an effective amount of a halide composition. Further alternative embodiments can include catalytic amounts of various co-catalyst combinations, such as lead, titanium, and platinum; lead, titanium, and cerium; lead, titanium, and iron; lead, titanium, and ytterbium; lead, titanium, and zinc; lead, titanium, and manganese; lead, titanium, and copper; lead, titanium, and europium; and lead, titanium, and bismuth. Additional embodiments can include catalytic amounts of the following co-catalyst combinations: lead and nickel; lead and zirconium; lead and iridium; lead and rhodium; lead and ruthenium; lead and chromium; lead and bismuth; lead and iron; lead and yttrium; lead, cerium, and manganese; lead, copper, and manganese; lead, iron, and manganese; lead, ytterbium, and manganese; lead, zinc, and manganese; lead, manganese, and europium; lead,

manganese, and bismuth; lead, iron, and copper; lead, cerium, and copper; lead, cerium, and iron; lead, cerium, and bismuth; and lead, cerium, and zinc.

BRIEF DESCRIPTION OF THE DRAWING

Various features, aspects, and advantages of the present invention will become more apparent with reference to the following description, appended claims, and accompanying drawing, wherein the FIGURE is a schematic view of a device capable of performing an aspect of an embodiment of the present invention.

DETAILED DESCRIPTION

The present invention is directed to a method and catalyst system for producing aromatic carbonates. In one embodiment, the method includes the step of contacting at least one aromatic hydroxy compound with oxygen and carbon monoxide in the presence of a carbonylation catalyst system that includes a catalytic amount of an inorganic co-catalyst containing lead and a catalytic amount of an inorganic co-catalyst containing titanium. In alternative embodiments, the catalyst system can include an effective amount of a Group VIII B metal and an effective amount of a halide composition.

Unless otherwise noted, the term "effective amount," as used herein, includes that amount of a substance capable of either increasing (directly or indirectly) the yield of the carbonylation product or increasing selectivity toward an aromatic carbonate. Optimum amounts of a given reactant can vary based on reaction conditions and the identity of other constituents yet can be readily determined in light of the discrete circumstances of a given application.

Aromatic hydroxy compounds which may be used in the practice of the present invention include aromatic mono or polyhydroxy compounds, such as phenol, cresol,

xilenol, resorcinol, hydroquinone, and bisphenol A. Aromatic organic mono hydroxy compounds are preferred, with phenol being more preferred.

In various preferred embodiments, the carbonylation catalyst system can contain at least one constituent from the Group VIII B metals or a compound thereof. A preferred Group VIII B constituent is an effective amount of a palladium source. In various embodiments, the palladium source may be in elemental form, or it may be employed as a palladium compound. Accordingly, palladium black or elemental palladium deposited on carbon may be used as well as palladium halides, nitrates, carboxylates, oxides and palladium complexes containing carbon monoxide, amines, phosphines or olefins. As used herein, the term "complexes" includes coordination or complex compounds containing a central ion or atom. The complexes may be nonionic, cationic, or anionic, depending on the charges carried by the central atom and the coordinated groups. Other common names for these complexes include complex ions (if electrically charged), Werner complexes, and coordination complexes.

In various applications, it may be preferable to utilize palladium(II) salts of organic acids, including carboxylates with C₂₋₆ aliphatic acids. Palladium(II) acetylacetonate is also a suitable palladium source. Preferably, the amount of Group VIII B metal source employed should be sufficient to provide about 1 mole of metal per 800-10,000 moles of aromatic hydroxy compound. More preferably, the proportion of Group VIII B metal source employed should be sufficient to provide about 1 mole of metal per 2,000-5,000 moles of aromatic hydroxy compound.

The carbonylation catalyst system may further contain an effective amount of a halide composition, such as an organic halide salt. In various preferred embodiments, the halide composition can be an organic bromide salt. The salt may be a quaternary ammonium or phosphonium salt, or a hexaalkylguanidinium bromide. In various embodiments, α , ω -bis(pentaalkylguanidinium)alkane salts may be preferred. Suitable organic halide compositions include tetrabutylammonium bromide,

tetraethylammonium bromide, and hexaethylguanidinium bromide. In preferred embodiments, the carbonylation catalyst system can contain between about 5 and about 1000 moles of bromide per mole of palladium employed, and, more preferably, between about 50 and about 150 molar equivalents of bromide are used.

The formation of diaryl carbonates in a carbonylation reaction can be accompanied by the formation of by-products, such as bisphenols, in varying proportions. In order to increase selectivity to diaryl carbonate, various organic co-catalysts may be incorporated in the carbonylation catalyst system. Depending on the application, suitable organic co-catalyst may include various phosphine, quinone, terpyridine, phenanthroline, quinoline and isoquinoline compounds and their derivatives, such as 2,2':6',2-terpyridine, 4'-methylthio-2,2':6',2-terpyridine, 2,2':6',2-terpyridine N-oxide, 1,10-phenanthroline, 2,4,7,8-tetramethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and 3,4,7,8-tetramethyl-1,10-phenanthroline.

The carbonylation catalyst system includes a catalytic amount of an inorganic co-catalyst (IOCC). In addition to lead and titanium per se, it has been discovered that certain IOCC combinations can effectively catalyze the carbonylation reaction. Such IOCC combinations include lead, titanium, and platinum; lead, titanium, and cerium; lead, titanium, and iron; lead, titanium, and ytterbium; lead, titanium, and zinc; lead, titanium, and manganese; lead, titanium, and copper; lead, titanium, and europium; and lead, titanium, and bismuth. Additional non-titanium embodiments include catalytic amounts of the following co-catalyst combinations: lead and nickel; lead and zirconium; lead and iridium; lead and rhodium; lead and ruthenium; lead and chromium; lead and bismuth; lead and iron; lead and yttrium; lead, cerium, and manganese; lead, copper, and manganese; lead, iron, and manganese; lead, ytterbium, and manganese; lead, zinc, and manganese; lead, manganese, and europium; lead, manganese, and bismuth; lead, iron, and copper; lead, cerium, and copper; lead, cerium, and iron; lead, cerium, and bismuth; and lead, cerium, and zinc.

An IOCC can be introduced to the carbonylation reaction in various forms, including salts and complexes, such as tetradentate, pentadentate, hexadentate, or octadentate

complexes. Illustrative forms may include oxides, halides, carboxylates, diketones (including beta-diketones), nitrates, complexes containing carbon monoxide or olefins, and the like. Suitable beta-diketones include those known in the art as ligands for the IOCC metals of the present invention. Examples include, but are not limited to, acetylacetone, benzoylacetone, dibenzoylmethane, diisobutyrylmethane, 2,2-dimethylheptane-3,5-dione, 2,2,6-trimethylheptane-3,5-dione, dipivaloylmethane, and tetramethylheptanedione. The quantity of ligand is preferably not such that it interferes with the carbonylation reaction itself, with the isolation or purification of the product mixture, or with the recovery and reuse of catalyst components (such as palladium). An IOCC may be used in its elemental form if sufficient reactive surface area can be provided. In embodiments employing supported palladium, it is noted that the IOCC provides a discrete, catalytic source of metal in a form favorable for such catalysis.

IOCC's are included in the carbonylation catalyst system in catalytic amounts. In this context a "catalytic amount" is an amount of IOCC (or combination of IOCC's) that increases the number of moles of aromatic carbonate produced per mole of Group VIII B metal utilized; increases the number of moles of aromatic carbonate produced per mole of halide utilized; or increases selectivity toward aromatic carbonate production beyond that obtained in the absence of the IOCC (or combination of IOCC's). Optimum amounts of an IOCC in a given application will depend on various factors, such as the identity of reactants and reaction conditions. For example, when palladium is included in the reaction, the molar ratio of lead relative to palladium at the initiation of the reaction is preferably between about 0.1 and about 100. Additional IOCC's may be used in the carbonylation catalyst system, provided the additional IOCC does not deactivate (i.e. "poison") the original IOCC.

The carbonylation reaction can be carried out in a batch reactor or a continuous reactor system. Due in part to the low solubility of carbon monoxide in organic hydroxy compounds, such as phenol, it is preferable that the reactor vessel be pressurized. In preferred embodiments, gas can be supplied to the reactor vessel in

proportions of between about 2 and about 50 mole percent oxygen, with the balance being carbon monoxide. Additional gases may be present in amounts that do not deleteriously affect the carbonylation reaction. The gases may be introduced separately or as a mixture. A total pressure in the range of between about 10 and about 250 atmospheres is preferred. Drying agents, typically molecular sieves, may be present in the reaction vessel. Reaction temperatures in the range of between about 60° C and about 150° C are preferred. Gas sparging or mixing can be used to aid the reaction.

In order that those skilled in the art will be better able to practice the present invention reference is made to the FIGURE, which shows an example of a continuous reactor system for producing aromatic carbonates. The symbol "V" indicates a valve and the symbol "P" indicates a pressure gauge.

The system includes a carbon monoxide gas inlet 10, an oxygen inlet 11, a manifold vent 12, and an inlet 13 for a gas, such as carbon dioxide. A reaction mixture can be fed into a low pressure reservoir 20, or a high pressure reservoir 21, which can be operated at a higher pressure than the reactor for the duration of the reaction. The system further includes a reservoir outlet 22 and a reservoir inlet 23. The gas feed pressure can be adjusted to a value greater than the desired reactor pressure with a pressure regulator 30. The gas can be purified in a scrubber 31 and then fed into a mass flow controller 32 to regulate flow rates. The reactor feed gas can be heated in a heat exchanger 33 having appropriate conduit prior to being introduced to a reaction vessel 40. The reaction vessel pressure can be controlled by a back pressure regulator 41. After passing through a condenser 25, the reactor gas effluent may be either sampled for further analysis at valve 42 or vented to the atmosphere at valve 50. The reactor liquid can be sampled at valve 43. An additional valve 44 can provide further system control, but is typically closed during the gas flow reaction.

In the practice of one embodiment of the invention, the carbonylation catalyst system and aromatic hydroxy compound are charged to the reactor system. The system is sealed. Carbon monoxide and oxygen are introduced into an appropriate reservoir

until a preferred pressure (as previously defined) is achieved. Circulation of condenser water is initiated, and the temperature of the heat exchanger 33 (e.g., oil bath) can be raised to a desired operating temperature. A conduit 46 between heat exchanger 33 and reaction vessel 40 can be heated to maintain the desired operating temperature. The pressure in reaction vessel 40 can be controlled by the combination of reducing pressure regulator 30 and back pressure regulator 41. Upon reaching the desired reactor temperature, aliquots can be taken to monitor the reaction.

EXAMPLES

The following examples are included to provide additional guidance to those skilled in the art in practicing the claimed invention. While some of the examples are illustrative of various embodiments of the claimed invention, others are comparative and are identified as such. The examples provided are merely representative of the work that contributes to the teaching of the present application. Accordingly, these examples are not intended to limit the invention, as defined in the appended claims, in any manner. Unless otherwise specified, all parts are by weight, and all equivalents are relative to palladium. Reaction products were verified by gas chromatography. All reactions were carried out in a glass, batch reactor at 90-100° C in a 10% O₂ in CO atmosphere at an operating pressure of 95-102 atm. Reaction time was generally 2-3 hours.

As discussed supra, the economics of aromatic carbonate production is dependent on the number of moles of aromatic carbonate produced per mole of Group VIII B metal utilized. In the following examples, the aromatic carbonate produced is diphenylcarbonate (DPC) and the Group VIII B metal utilized is palladium. For convenience, the number of moles of DPC produced per mole of palladium utilized is referred to as the palladium turnover number (Pd TON).

BASELINE EXAMPLE

In order to determine the comparative efficacy of various embodiments of the present invention, baseline data were produced by adding, at ambient conditions, 0.25 mM palladium(II) acetylacetonate and various amounts of halide compositions to a glass reaction vessel containing phenol. The reactants were heated to 100°C for 3 hours in a 10 % oxygen in carbon monoxide atmosphere. After the reaction, samples were analyzed for DPC by gas chromatography producing the following results:

Experiment No.	Pd ppm	HegBr Equivalents	Pd TON
1	25	0	82.3
2	25	30	75.5
3	25	60	50.3
4	25	120	46.3
5	25	240	44.2
6	25	600	38.7

EXAMPLE 1

Diphenyl carbonate was produced by adding, at ambient conditions, .25 mM palladium(II) acetylacetonate, hexaethylguanidinium bromide ("HegBr"), and an inorganic co-catalyst combination of lead(II) oxide and titanium(IV) oxide acetylacetonate to a glass reaction vessel containing phenol. The reactants were heated to 100°C for 3 hours in a 10 % oxygen in carbon monoxide atmosphere. After

the reaction, samples were analyzed for DPC by gas chromatography. The following results were observed:

Experiment No.	PbO Equivalents	Ti(O) ₂ Equivalents	HegBr Equivalents	Pd TON
1	12	2	600	1162
2	12	5	600	1100
3	12	12	600	1255

The procedure was repeated with various amounts of inorganic co-catalysts supplied in the acetylacetonate form to provide the following results:

Experiment No.	PbO Equivalents	TiO(acac) ₂ Equivalents	HegBr Equivalents	Pd TON
4	2.8	14	120	1248
5	2.8	14	30	463
6	5.6	28	120	992
7	5.6	28	30	872
8	14	14	60	1227
9	14	2.8	120	1348
10	14	2.8	30	570

Experiment No.	PbO Equivalents	TiO(acac) ₂ Equivalents	HegBr Equivalents	Pd TON
11	28	5.6	120	2076
12	28	5.6	30	487

The procedure was repeated with tetrabutylammonium chloride as a halide source to produce the following results:

Experiment No.	PbO Equivalents	TiO(acac) ₂ Equivalents	TBACl Equivalents	Pd TON
13	12	12	100	603
14	12	12	400	623

The various reaction conditions show that a Pd TON at least as high as 2076 can be obtained utilizing the combination of lead and titanium as an IOCC. Based on the results of these experiments, it is evident that an IOCC containing lead and titanium can effectively catalyze the carbonylation reaction.

EXAMPLE 2

The general procedure of Example 1 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate and 14 equivalents of nickel in the form of nickel(II)

acetylacetonate. The Pd TON was found to be 162, thus showing that the IOCC combination of lead and nickel can effectively catalyze the carbonylation reaction.

The procedure was repeated with lead supplied in the form of lead oxide with the following results:

Experiment No.	PbO Equivalents	Ni(acac) ₂ Equivalents	HegBr Equivalents	Pd TON
1	12	2	600	1013
2	12	5	600	1071
3	12	12	600	1089

EXAMPLE 3

The general procedure of Examples 1 and 2 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of hexaethylguanidinium bromide, and various amounts of lead and zirconium as an IOCC combination to provide the following results:

Experiment No.	PbO Equivalents	Zr(acac) ₄ Equivalents	HegBr Equivalents	Pd TON
1	12	2	600	931
2	12	5	600	778

3	12	12	600	659
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The results show that the IOCC combination of lead and zirconium can effectively catalyze the carbonylation reaction.

EXAMPLE 4

The general procedure of Examples 1-3 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of hexaethylguanidinium bromide, and various amounts of a lead(II) and iridium(III) as an IOCC combination to provide the following results:

Experiment No.	PbO Equivalents	Ir(acac) ₃ Equivalents	HegBr Equivalents	Pd TON
1	12	2	600	587
2	12	5	600	509
3	12	12	600	542

Based on the results of these experiments it is evident that the IOCC combination of lead and iridium can effectively catalyze the carbonylation reaction.

EXAMPLE 5

The general procedure of Examples 1-4 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of hexaethylguanidinium bromide, and various amounts of a lead(II) and rhodium(III) as an IOCC combination to provide the following results:

Experiment No.	PbO Equivalents	Rh(acac) ₃ Equivalents	HegBr Equivalents	Pd TON
1	12	2	600	559
2	12	5	600	530
3	12	12	600	559

Based on the results of these experiments it is evident that the IOCC combination of lead and rhodium can effectively catalyze the carbonylation reaction

EXAMPLE 6

The general procedure of Examples 1-5 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of hexaethylguanidinium bromide, and various amounts of a lead(II) and ruthenium(III) as an IOCC combination to provide the following results:

Experiment No.	PbO Equivalents	Ru(acac) ₃ Equivalents	HegBr Equivalents	Pd TON

1	12	2	600	514
2	12	5	600	278
3	12	12	600	227

Based on the results of these experiments it is evident that the IOCC combination of lead and ruthenium can effectively catalyze the carbonylation reaction

EXAMPLE 7

The general procedure of Examples 1-6 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate and 14 equivalents of chromium in the form of chromium(III) acetylacetonate. The Pd TON was found to be 224, thus showing that the IOCC combination of lead and chromium can effectively catalyze the carbonylation reaction.

EXAMPLE 8

The general procedure of Examples 1-7 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate and 14 equivalents of bismuth in the form of bismuth(II)tetramethylheptanedionate. The Pd TON was found to be 360, thus showing that the IOCC combination of lead and bismuth can effectively catalyze the carbonylation reaction.

The procedure was repeated with 108 equivalents of bromide in the form of tetraethylammonium bromide and the IOCC combination of 9.8 equivalents of lead in the form of lead(II) oxide and 10.2 equivalents of bismuth in the form of bismuth(III)bromide. The Pd TON was found to be 443.

EXAMPLE 9

The general procedure of Examples 1-8 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 25 ppm platinum(II) acetylacetonate. The Pd TON was found to be 1284, thus showing that the IOCC combination of lead, titanium, and platinum can effectively catalyze the carbonylation reaction.

EXAMPLE 10

The general procedure of Examples 1-9 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate and 14 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 565.

The reaction was repeated with 25 ppm palladium(II) acetylacetonate and various concentrations of bromide and IOCC to provide the following results:

Experiment No.	Pb(acac) ₂	Fe(acac) ₃	HegBr	Pd TON

	Equivalents	Equivalents	Equiv.	
1	2.8	14	120	117
2	2.8	14	30	334
3	5.6	28	120	194
4	5.6	28	30	448
5	14	2.8	120	889
6	14	2.8	30	239
7	28	5.6	120	654
8	28	5.6	30	214

These results show that a Pd TON at least as high as 889 can be obtained utilizing the IOCC combination of lead and iron. Consequently, it is evident that this IOCC combination can effectively catalyze the carbonylation reaction.

EXAMPLE 11

The general procedure of Examples 1-10 was repeated with 25 ppm palladium(II) acetylacetonate, 100 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 25 equivalents of lead in the form of lead(II) oxide and 11 equivalents of yttrium in the form of yttrium(III) acetylacetonate. The Pd TON was found to be 1226, thus showing that the IOCC combination of lead and yttrium can effectively catalyze the carbonylation reaction.

EXAMPLE 12

The general procedure of Examples 1-11 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of cerium in the form of cerium(III) acetylacetonate. The Pd TON was found to be 1401, thus showing that the IOCC combination of lead, titanium, and cerium can effectively catalyze the carbonylation reaction.

EXAMPLE 13

The general procedure of Examples 1-12 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 1631, thus showing that the IOCC combination of lead, titanium, and iron can effectively catalyze the carbonylation reaction.

EXAMPLE 14

The general procedure of Examples 1-13 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of ytterbium in the form of ytterbium(III) acetylacetonate. The Pd TON was found to be 1206, thus showing that the IOCC combination of lead, titanium, and ytterbium can effectively catalyze the carbonylation reaction.

EXAMPLE 15

The general procedure of Examples 1-14 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of zinc in the form of zinc(II) acetylacetonate. The Pd TON was found to be 1310, thus showing that the IOCC combination of lead, titanium, and zinc can effectively catalyze the carbonylation reaction.

EXAMPLE 16

The general procedure of Examples 1-15 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of manganese in the form of manganese(III) acetylacetonate. The Pd TON was found to be 1237, thus showing that the IOCC combination of lead, titanium, and manganese can effectively catalyze the carbonylation reaction.

The reaction was repeated with 23 mM palladium(II) acetylacetonate and various amounts of bromide and IOCC to provide the following results:

Experiment	Pb(acac) ₂	Mn(acac) ₃	TiO(acac) ₂	HegBr	Pd TON
No.	Equiv.	Equiv.	Equiv.	Equiv.	

1	28	2	1	120	1632
2	28	2	4	120	1535
3	28	2	8	120	1463
4	28	4	1	120	1565
5	28	4	4	120	1688
6	28	4	8	120	1391
7	28	8	1	120	1267
8	28	8	4	120	1509
9	28	8	8	120	1518
10	56	2	1	120	1154
11	56	2	4	120	1377
12	56	2	8	120	1678
13	56	4	1	120	1256
14	56	4	4	120	1400
15	56	4	8	120	1419
16	56	8	1	120	1242
17	56	8	4	120	1405
18	56	8	8	120	1444

The various reaction conditions show that a Pd TON at least as high as 1688 can be obtained utilizing the combination of lead, manganese, and titanium as an IOCC.

EXAMPLE 17

The general procedure of Examples 1-16 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of cerium in the form of cerium(III) acetylacetonate, and 14 equivalents of manganese in the form of manganese(III) acetylacetonate. The Pd TON was found to be 921, thus showing that the IOCC combination of lead, cerium, and manganese can effectively catalyze the carbonylation reaction.

EXAMPLE 18

The general procedure of Examples 1-17 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III) acetylacetonate, and 14 equivalents of copper in the form of copper(II) acetylacetonate. The Pd TON was found to be 1094, thus showing that the IOCC combination of lead, manganese, and copper can effectively catalyze the carbonylation reaction.

EXAMPLE 19

The general procedure of Examples 1-18 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III)

acetylacetonate, and 14 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 1098, thus showing that the IOCC combination of lead, manganese, and iron can effectively catalyze the carbonylation reaction.

EXAMPLE 20

The general procedure of Examples 1-19 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III) acetylacetonate, and 14 equivalents of ytterbium in the form of ytterbium(III) acetylacetonate. The Pd TON was found to be 1048, thus showing that the IOCC combination of lead, manganese, and ytterbium can effectively catalyze the carbonylation reaction.

EXAMPLE 21

The general procedure of Examples 1-20 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III) acetylacetonate, and 14 equivalents of zinc in the form of zinc(II) acetylacetonate. The Pd TON was found to be 888, thus showing that the IOCC combination of lead, manganese, and zinc can effectively catalyze the carbonylation reaction.

EXAMPLE 22

The general procedure of Examples 1-21 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of copper in the form of copper(II) acetylacetonate. The Pd TON was found to be 393, thus showing that the IOCC combination of lead, titanium, and copper can effectively catalyze the carbonylation reaction.

EXAMPLE 23

The general procedure of Examples 1-22 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III) acetylacetonate, and 14 equivalents of europium in the form of europium(III) acetylacetonate. The Pd TON was found to be 1235, thus showing that the IOCC combination of lead, manganese, and europium can effectively catalyze the carbonylation reaction.

EXAMPLE 24

The general procedure of Examples 1-23 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of manganese in the form of manganese(III) acetylacetonate, and 14 equivalents of bismuth in the form of bismuth(II)tetramethylheptanedionate. The Pd TON was found to be 683, thus

showing that the IOCC combination of lead, manganese, and bismuth can effectively catalyze the carbonylation reaction.

EXAMPLE 25

The general procedure of Examples 1-24 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of iron in the form of iron(III) acetylacetonate, and 14 equivalents of copper in the form of copper(II) acetylacetonate. The Pd TON was found to be 449, thus showing that the IOCC combination of lead, iron, and copper can effectively catalyze the carbonylation reaction.

EXAMPLE 26

The general procedure of Examples 1-25 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of europium in the form of europium(III) acetylacetonate. The Pd TON was found to be 990, thus showing that the IOCC combination of lead, titanium, and europium can effectively catalyze the carbonylation reaction.

EXAMPLE 27

The general procedure of Examples 1-26 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate, and 14 equivalents of bismuth in the form of bismuth(II)tetramethylheptanedionate. The Pd TON was found to be 873, thus showing that the IOCC combination of lead, titanium, and bismuth can effectively catalyze the carbonylation reaction.

EXAMPLE 28

The general procedure of Examples 1-27 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of cerium in the form of cerium(III) acetylacetonate, and 14 equivalents of copper in the form of copper(II) acetylacetonate. The Pd TON was found to be 858, thus showing that the IOCC combination of lead, cerium, and copper can effectively catalyze the carbonylation reaction.

EXAMPLE 29

The general procedure of Examples 1-28 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of cerium in the form of cerium(III) acetylacetonate, and 14 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 1002, thus showing that the IOCC combination of lead, cerium, and iron can effectively catalyze the carbonylation reaction.

EXAMPLE 30

The general procedure of Examples 1-29 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of cerium in the form of cerium(III) acetylacetonate, and 14 equivalents of bismuth in the form of bismuth(II)tetramethylheptanedionate. The Pd TON was found to be 635, thus showing that the IOCC combination of lead, cerium, and bismuth can effectively catalyze the carbonylation reaction.

EXAMPLE 31

The general procedure of Examples 1-30 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate, 14 equivalents of cerium in the form of cerium(III) acetylacetonate, and 14 equivalents of zinc in the form of zinc(II) acetylacetonate. The Pd TON was found to be 860, thus showing that the IOCC combination of lead, cerium, and zinc can effectively catalyze the carbonylation reaction.

COMPARATIVE EXAMPLE A

It has been determined that several potential IOCC candidates do not catalyze the carbonylation reaction and in fact may poison an otherwise effective IOCC combination. For example, the general procedure of Examples 1-31 was repeated with 25 mM palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and 14 equivalents of antimony in the form of

antimony(III)bromide as a potential IOCC candidate. The Pd TON was found to be zero, thereby showing that Sb(III) does not effectively catalyze the carbonylation reaction at the conditions used.

COMPARATIVE EXAMPLE B

The general procedure of Examples 1-31 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and the following IOCC combination: 14 equivalents of lead in the form of lead(II) acetylacetonate and 14 equivalents of antimony in the form of SbBr₃. The Pd TON was found to be zero, thereby showing that, in addition to failing to effectively catalyze the carbonylation reaction as a sole IOCC, Sb(III) can poison an otherwise effective IOCC (i.e. lead) at the conditions used.

COMPARATIVE EXAMPLE C

The general procedure of Examples 1-31 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of tetraethylammonium bromide, and 12 equivalents of vanadium in the form of vanadium(III) acetylacetonate as a potential IOCC candidate. The Pd TON was found to be zero, thereby showing that V(III) does not effectively catalyze the carbonylation reaction at the conditions used.

COMPARATIVE EXAMPLE D

The general procedure of Examples 1-31 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 12 equivalents of lead in the form of

lead(II) oxide and 12 equivalents of vanadium in the form of vanadium(III) acetylacetonate. The Pd TON was found to be zero, thereby showing that, in addition to failing to effectively catalyze the carbonylation reaction as a sole IOCC, V(III) can poison an otherwise effective IOCC (i.e. lead) at the conditions used.

COMPARATIVE EXAMPLE E

The general procedure of Examples 1-31 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of tetraethylammonium bromide, and 12 equivalents of tin in the form of tin(IV) bisacetylacetonatedibromide as a potential IOCC candidate. The Pd TON was found to be zero, thereby showing that Sn(IV) does not effectively catalyze the carbonylation reaction at the conditions used.

COMPARATIVE EXAMPLE F

The general procedure of Examples 1-31 was repeated with 25 ppm palladium(II) acetylacetonate, 600 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 12 equivalents of lead in the form of lead(II) oxide and 12 equivalents of tin in the form of tin(IV) bisacetylacetonate dibromide. The Pd TON was found to be zero, thereby showing that, in addition to failing to effectively catalyze the carbonylation reaction as a sole IOCC, Sn(IV) can poison an otherwise effective IOCC (i.e. lead) at the conditions used.

It will be understood that each of the elements described above, or two or more together, may also find utility in applications differing from the types described herein. While the invention has been illustrated and described as embodied in a method and catalyst system for producing aromatic carbonates, it is not intended to be

limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present invention. For example, additional effective IOCC compounds can be added to the reaction. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.

CLAIMS

What is claimed is:



1. A carbonylation catalyst system, comprising a catalytic amount of a combination of inorganic co-catalysts comprising lead and titanium.
2. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises platinum.
3. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises cerium.
4. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises iron.
5. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises ytterbium.
6. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises manganese.

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7. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises zinc.



8. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises bismuth.

9. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises europium.

10. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises copper.

11. The carbonylation catalyst system of claim 1, further comprising an effective amount of a palladium source.

12. The carbonylation catalyst system of claim 11, wherein the palladium source is a Pd(II) salt or complex.

13. The carbonylation catalyst system of claim 12, wherein the palladium source is palladium acetylacetonate.

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14. The carbonylation catalyst system of claim 11, wherein the palladium source is supported Pd.



15. The carbonylation catalyst system of claim 14, wherein the palladium source is palladium on carbon.

16. The carbonylation catalyst system of claim 11, further comprising an effective amount of a halide composition.

17. The carbonylation catalyst system of claim 16, wherein the halide composition is tetraethylammonium bromide.

18. The carbonylation catalyst system of claim 16, wherein the halide composition is hexaethylguanidinium bromide.

19. The carbonylation catalyst system of claim 11, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.

20. The carbonylation catalyst system of claim 1, wherein the combination of inorganic co-catalysts further comprises a substance selected from the group consisting of platinum; cerium; iron; ytterbium; zinc; manganese; copper; europium; and bismuth.



21. The carbonylation catalyst system of claim 20, further comprising an effective amount of a palladium source.



22. The carbonylation catalyst system of claim 21, wherein the palladium source is a Pd(II) salt or complex.

23. The carbonylation catalyst system of claim 22, wherein the palladium source is palladium acetylacetonate.

24. The carbonylation catalyst system of claim 21, wherein the palladium source is supported Pd.

25. The carbonylation catalyst system of claim 24, wherein the palladium source is palladium on carbon.

26. The carbonylation catalyst system of claim 21, further comprising an effective amount of a halide composition.

27. The carbonylation catalyst system of claim 26, wherein the halide composition is tetraethylammonium bromide.

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28. The carbonylation catalyst system of claim 26, wherein the halide composition is hexaethylguanidinium bromide.



29. The carbonylation catalyst system of claim 21, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.

30. A carbonylation catalyst system, comprising a catalytic amount of a combination of inorganic co-catalysts comprising lead and a substance selected from the group consisting of nickel; zirconium; iridium; rhodium; ruthenium; chromium; bismuth; iron; yttrium; cerium and manganese; copper and manganese; iron and manganese; ytterbium and manganese; zinc and manganese; manganese and europium; manganese and bismuth; iron and copper; cerium and copper; cerium and iron; cerium and bismuth; and cerium and zinc.

31. The carbonylation catalyst system of claim 30, comprising a catalytic amount of an inorganic co-catalyst combination comprising lead, manganese, and europium.

32. The carbonylation catalyst system of claim 30, further comprising an effective amount of a palladium source.

33. The carbonylation catalyst system of claim 32, wherein the palladium source is a Pd(II) salt or complex.

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34. The carbonylation catalyst system of claim 33, wherein the palladium source is palladium acetylacetonate.

35. The carbonylation catalyst system of claim 32, wherein the palladium source is supported Pd.



36. The carbonylation catalyst system of claim 35, wherein the palladium source is palladium on carbon.

37. The carbonylation catalyst system of claim 32, further comprising an effective amount of a halide composition.

38. The carbonylation catalyst system of claim 37, wherein the halide composition is tetraethylammonium bromide.

39. The carbonylation catalyst system of claim 37, wherein the halide composition is hexaethylguanidinium bromide.

40. The carbonylation catalyst system of claim 32, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.

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41. A method of carbonylating aromatic hydroxy compounds, said method comprising the step of:

contacting at least one aromatic hydroxy compound with oxygen and carbon monoxide in the presence of a carbonylation catalyst system comprising a catalytic amount of a combination of inorganic co-catalysts comprising lead and titanium.

42. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises platinum.



43. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises cerium.

44. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises iron.

45. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises ytterbium.

46. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises manganese.

47. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises zinc.



48. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises bismuth.

49. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises europium.



50. The method of claim 41, wherein the combination of inorganic co-catalysts further comprises copper.

51. The method of claim 41, wherein the carbonylation catalyst system further comprises an effective amount of a palladium source.

52. The method of claim 51, wherein the palladium source is a Pd(II) salt or complex.

53. The method of claim 52, wherein the palladium source is palladium acetylacetonate.

54. The method of claim 51, wherein the palladium source is supported Pd.

55. The method of claim 54, wherein the palladium source is palladium on carbon.

56. The method of claim 51, wherein the carbonylation catalyst system further comprises an effective amount of a halide composition.

57. The method of claim 56, wherein the halide composition is tetraethylammonium bromide.



58. The method of claim 56, wherein the halide composition is hexaethylguanidinium bromide.

59. The method of claim 41, wherein the aromatic hydroxy compound is phenol.

60. The method of claim 51, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.

61. The method of claim 41, wherein the carbonylation catalyst system further comprises a substance selected from the group consisting of platinum; cerium; iron; ytterbium; zinc; manganese; copper; europium; and bismuth.

62. The method of claim 61, wherein the carbonylation catalyst system further comprises an effective amount of a palladium source.

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63. The method of claim 62, wherein the palladium source is a Pd(II) salt or complex.

64. The method of claim 63, wherein the palladium source is palladium acetylacetonate.



65. The method of claim 62, wherein the palladium source is supported Pd.

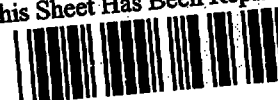
66. The method of claim 65, wherein the palladium source is palladium on carbon.

67. The method of claim 62, wherein the carbonylation catalyst system further comprises an effective amount of a halide composition.

68. The method of claim 67, wherein the halide composition is tetraethylammonium bromide.

69. The method of claim 67, wherein the halide composition is hexaethylguanidinium bromide.

70. The method of claim 61, wherein the aromatic hydroxy compound is phenol.



71. The method of claim 62, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.



72. A method of carbonylating aromatic hydroxy compounds, said method comprising the step of:

contacting at least one aromatic hydroxy compound with oxygen and carbon monoxide in the presence of a carbonylation catalyst system

comprising a catalytic amount of a combination of inorganic co-catalysts comprising lead and a substance selected from the group consisting of nickel; zirconium; iridium; rhodium; ruthenium; chromium; bismuth; iron; yttrium; cerium and manganese; copper and manganese; iron and manganese; ytterbium and manganese; zinc and manganese; manganese and europium; manganese and bismuth; iron and copper; cerium and copper; cerium and iron; cerium and bismuth; and cerium and zinc.

73. The method of claim 72, wherein the carbonylation catalyst system comprises a catalytic amount of an inorganic co-catalyst combination comprising lead, manganese, and europium.

74. The method of claim 72, wherein the carbonylation catalyst system further comprises an effective amount of a palladium source.

75. The method of claim 74, wherein the palladium source is a Pd(II) salt or complex.



76. The method of claim 75, wherein the palladium source is palladium acetylacetonate.



77. The method of claim 74, wherein the palladium source is supported Pd.

78. The method of claim 77, wherein the palladium source is palladium on carbon.

79. The method of claim 74, wherein the carbonylation catalyst system further comprises an effective amount of a halide composition.

80. The method of claim 79, wherein the halide composition is tetraethylammonium bromide.

81. The method of claim 79, wherein the halide composition is hexaethylguanidinium bromide.

82. The method of claim 72, wherein the aromatic hydroxy compound is phenol.

83. The method of claim 74, wherein the molar ratio of lead relative to palladium is between about 0.1 and about 100.

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