

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 zinc.

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 zinc and copper; zinc, copper, and titanium; zinc, copper and iron; zinc and cerium; zinc and manganese; zinc, manganese, and europium; zinc, manganese, and bismuth; zinc and europium; zinc and nickel; zinc and iron; zinc and cobalt; zinc and ruthenium; zinc and rhodium; zinc and zirconium; and zinc and chromium.

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 zinc. 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, xylenol, 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) containing zinc. In addition to zinc per se, it has been discovered that certain IOCC combinations can effectively catalyze the carbonylation reaction. Such IOCC combinations include zinc and copper; zinc, copper, and titanium; zinc, copper and iron; zinc and cerium; zinc and manganese; zinc, manganese, and europium; zinc, manganese, and bismuth; zinc and europium; zinc and nickel; zinc and iron; zinc and cobalt; zinc and ruthenium; zinc and rhodium; zinc and zirconium; and zinc and chromium.

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 zinc-based IOCC provides a discrete, catalytic source of zinc 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 zinc 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. Examples of additional IOCC's may include lead and/or iridium.

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, palladium(II) acetylacetonate, hexaethylguanidinium bromide ("HegBr"), and zinc(II) acetylacetonate as an inorganic co-catalyst 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.	Pd Ppm	Zn Equivalents Zn(acac) ₂	Br Equivalents HegBr	Pd TON
1	25	6.7	187	208
2	25	14	60.0	683
3	25	17	562	271

The procedure was repeated with various zinc complexes using various bromide amounts to produce the following results:

Experiment No.	Pd Ppm	Zn Equivalents zinc stearate	Br Equivalents HegBr	Pd TON
4	25	10	289	138
5	25	50	289	329
6	25	10	578	164
7	25	50	578	291

Experiment No.	Pd Ppm	Zn Equivalents zinc acetate	Br Equivalents HegBr	Pd TON
8	25	6.7	187	212
9	25	17	562	274

The various reaction conditions show that a Pd TON at least as high as 683 can be obtained utilizing zinc as an IOCC. Based on the results of these experiments, it is evident that an IOCC containing zinc can effectively catalyze the carbonylation reaction.

EXAMPLE 2

The general procedure of Example 1 was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 9 equivalents of copper in the form of copper(II) acetylacetonate. The Pd TON was found to be 1219, thus showing that the IOCC combination of zinc and copper can effectively catalyze the carbonylation reaction.

EXAMPLE 3

The general procedure of Examples 1 and 2 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 zinc in the form of zinc(II) acetylacetonate, 14 equivalents of copper in the form of copper(II) acetylacetonate, and 14 equivalents of titanium in the form of titanium(IV) oxide acetylacetonate. The Pd TON was found to be 1145, thus showing that the IOCC combination of zinc, copper, and titanium can effectively catalyze the carbonylation reaction.

EXAMPLE 4

The general procedure of Examples 1-3 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 zinc in the form of zinc(II) acetylacetonate, 14 equivalents of copper in the form of copper(II) acetylacetonate, and 14 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 1141, thus showing that the IOCC combination of zinc, copper, and iron can effectively catalyze the carbonylation reaction.

EXAMPLE 5

The general procedure of Examples 1-4 was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 9 equivalents of cerium in the form of cerium(III) acetylacetonate. The Pd TON was found to be 1284, thus showing that the IOCC combination of zinc and cerium can effectively catalyze the carbonylation reaction.

EXAMPLE 6

The general procedure of Examples 1-5 was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 10 equivalents of manganese in the form of manganese(II) acetylacetonate. The Pd TON was found to be 1876, thus showing that the IOCC combination of zinc and manganese 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 zinc in the form of zinc(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 782, thus showing that the IOCC

combination of zinc, manganese, and europium 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 zinc in the form of zinc(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 452, thus showing that the IOCC combination of zinc, manganese, and bismuth can effectively catalyze the carbonylation reaction.

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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of europium in the form of europium(III) acetylacetonate. The Pd TON was found to be 448, thus showing that the IOCC combination of zinc and europium 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of nickel in the form of nickel(II) acetylacetonate. The Pd TON was found to be 298, thus showing that the IOCC combination of zinc and nickel can effectively catalyze the carbonylation reaction.

The experiment was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 11 equivalents of nickel in the form of nickel(II) acetylacetonate. The Pd TON was found to be 1017.

EXAMPLE 11

The general procedure of Examples 1-10 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of chromium in the form of chromium(III) acetylacetonate. The Pd TON was found to be 401, thus showing that the IOCC combination of zinc and chromium can effectively catalyze the carbonylation reaction.

The experiment was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 8 equivalents of chromium in the form of chromium(III) acetylacetonate. The Pd TON was found to be 674.

EXAMPLE 12

The general procedure of Examples 1-11 was repeated with 25 ppm palladium(II) acetylacetonate, 123 equivalents of bromide in the form of tetraethylammonium bromide, and the following IOCC combination: 11 equivalents of zinc in the form of zinc(II) acetylacetonate and 9 equivalents of iron in the form of iron(III) acetylacetonate. The Pd TON was found to be 969, thus showing that the IOCC combination of zinc and iron 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of cobalt in the form of cobalt(III) acetylacetonate. The Pd TON was found to be 205, thus showing that the IOCC combination of zinc and cobalt 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of ruthenium in the form of ruthenium(III) acetylacetonate. The Pd TON was found to be 367, thus showing that the IOCC combination of zinc and ruthenium 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of rhodium in the form of rhodium(III) acetylacetonate. The Pd TON was found to be 488, thus showing that the IOCC combination of zinc and rhodium 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of zirconium in the form of zirconium(IV) acetylacetonate. The Pd TON was found to be 167, thus showing that the IOCC combination of zinc and zirconium 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 1-16 was repeated with 25 ppm 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 1-16 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 zinc in the form of zinc(II) acetylacetonate and 14 equivalents of antimony in the form of SbBr_3 . 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. zinc) at the conditions used.

COMPARATIVE EXAMPLE C

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 14 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 1-16 was repeated with 25 ppm palladium(II) acetylacetonate, 60 equivalents of bromide in the form of hexaethylguanidinium bromide, and 14 equivalents of vanadium in the form of vanadium(IV) oxide acetylacetonate as a potential IOCC candidate. The Pd TON was found to be zero, thereby showing that V(IV) does not effectively catalyze the carbonylation reaction 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 an inorganic co-catalyst comprising zinc.
2. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and copper.
3. The carbonylation catalyst system of claim 2, wherein the combination of inorganic co-catalysts further comprises titanium.
4. The carbonylation catalyst system of claim 2, wherein the combination of inorganic co-catalysts further comprises iron.
5. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and cerium.
6. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and manganese.



7. The carbonylation catalyst system of claim 6, wherein the combination of inorganic co-catalysts further comprises europium.
8. The carbonylation catalyst system of claim 6, wherein the combination of inorganic co-catalysts further comprises bismuth.
9. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and europium.
10. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and nickel.
11. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and zirconium.
12. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and iron.
13. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and cobalt.



14. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and ruthenium.
15. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and rhodium.
16. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and chromium.
17. The carbonylation catalyst system of claim 1, comprising a catalytic amount of a combination of inorganic co-catalysts comprising zinc and a substance selected from the group consisting of copper; copper and titanium; copper and iron; cerium; manganese; manganese and europium; manganese and bismuth; europium; nickel; iron; cobalt; ruthenium; rhodium; zirconium; and chromium.
18. The carbonylation catalyst system of claim 17, further comprising an effective amount of a palladium source.
19. The carbonylation catalyst system of claim 18, wherein the palladium source is a Pd(II) salt or complex.
20. The carbonylation catalyst system of claim 19, wherein the palladium source is palladium acetylacetonate.



21. The carbonylation catalyst system of claim 18, wherein the palladium source is supported Pd.
22. The carbonylation catalyst system of claim 21, wherein the palladium source is palladium on carbon.
23. The carbonylation catalyst system of claim 18, further comprising an effective amount of a halide composition.
24. The carbonylation catalyst system of claim 23, wherein the halide composition is tetraethylammonium bromide.
25. The carbonylation catalyst system of claim 23, wherein the halide composition is hexaethylguanidinium bromide.
26. The carbonylation catalyst system of claim 18, wherein the molar ratio of zinc relative to palladium is between about 0.1 and about 100.
27. 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 an inorganic co-catalyst comprising zinc.

28. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and copper.

29. The method of claim 28, wherein the combination of inorganic co-catalysts further comprises titanium.

30. The method of claim 28, wherein the combination of inorganic co-catalysts further comprises iron.

31. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and cerium.

32. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and manganese.



33. The method of claim 32, wherein the combination of inorganic co-catalysts further comprises europium.

34. The method of claim 32, wherein the combination of inorganic co-catalysts further comprises bismuth.

35. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and europium.

36. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and nickel.

37. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and zirconium.

38. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and iron.



39. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and cobalt.

40. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and ruthenium.

41. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and rhodium.

42. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and chromium.

43. The method of claim 27, wherein the carbonylation catalyst system comprises a catalytic amount of a combination of inorganic co-catalysts comprising zinc and a substance selected from the group consisting of copper; copper and titanium; copper and iron; cerium; manganese; manganese and europium; manganese and bismuth; europium; nickel; iron; cobalt; ruthenium; rhodium; zirconium; and chromium.

44. The method of claim 43, wherein the carbonylation catalyst system further comprises an effective amount of a palladium source.



45. The method of claim 44, wherein the palladium source is a Pd(II) salt or complex.
46. The method of claim 45, wherein the palladium source is palladium acetylacetonate.
47. The method of claim 44, wherein the palladium source is supported palladium.
48. The method of claim 47, wherein the supported palladium is palladium on carbon.
49. The method of claim 44, wherein the carbonylation catalyst system further comprises an effective amount of a halide composition.
50. The method of claim 49, wherein the halide composition is tetraethylammonium bromide.
51. The method of claim 49, wherein the halide composition is hexaethylguanidinium bromide.
52. The method of claim 43, wherein the aromatic hydroxy compound is phenol.



53. The method of claim 44, wherein the molar ratio of zinc relative to palladium is between about 0.1 and about 100 at the initiation of the carbonylation.

This Sheet Has Been Replaced

