1995, *491*, 11. Conia, J. M.; Leriverend, M. L. *Tetrahedron Letters. 1968*, *17*. 2101 (Conia et al.). L. Rand and R. J. Dolinski, *J. Org. Chem*., 1966, 31, 3063 and L. Rand and R. J. Dolinski, *J. Org. Chem*., 1966, 31, 4061 (collectively "Rand and Dolinski"). Yokota, K.; Kohsaka, T.; Ito, K.; Ishihara, N. Consideration of Mechanism of Styrene/Ethylene Copolymerization with Half-Titanocene Catalysts. *Journal of Polymer Science.* 2005, *43*, 5041. JP10316694A to Tetsuya, I., et. al. Brancaccio G.; Lettieri, G.; Monforte, P.; Larizza, A. *Farmaco, Edizione Scientifica.* 1983, 9, 702-8. Eaton, P. E.; Carlson, G. R.; Lee, J. T. Phosphorus Pentoxide-Methanesulfonic Acid. A Convenient Alternative to Polyphosphoric Acid. *J.Org. Chem*. 1978, *38*, 4071. Paquette, L. A.; Stevens, K. E., *Can. J. Chem.* 1984, *62*, 2415. Paquette, L. A.; Cheney, D. L., *J. Org. Chem.* 1989, *54*, 3334. *J.Org. Chem*. 1966, 3065.

[0005] Conia, et al. reported that reacting cyclohexene and crotonic acid in presence of polyphosphoric acid (PPA) exclusively gave as a sole product 2,3,4,5,6,7-hexahydro-3-methyl-1H-inden-1-one (structure 1 in Conia et al.). Conia et al. reported reacting cyclopentyl crotonate or cyclohexyl crotonate in the presence of PPA gave 3-methyl-bicyclo[3.3.0]-2-octen-1-one (40% yield, Table 1 in Conia et al.) or 2,3,4,5,6,7-hexahydro-3-methyl-1H-inden-1-one (60% yield, Table 2 in Conia et al.), respectively.

[0006] Rand and Dolinski report that using polyphosphoric acid (PPA) or a mixture of phosphorous pentoxide (P_2O_5 or P_4O_{10}) and PPA to catalyze the reaction of a cycloheptene, cyclohexene, or cyclopentene with an alpha,beta-unsaturated carboxylic acid such as acrylic acid or crotonic acid gives a reaction mixture that contains or is free of an ester by-product such as cycloheptyl crotonate, cyclohexyl crotonate, or cyclopentyl crotonate. Relatively how much of the ester by-product is made is said to depend on the amount of phosphorous pentoxide used in the mixture with PPA or the amount of the PPA or P_2O_5/PPA mixture relative to the amount of cycloalkene.

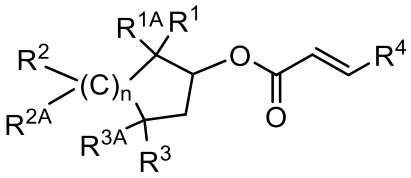
SUMMARY

[0007] We discovered cyclopentenone compounds ("cyclopentenones") are useful intermediates for making substituted cyclopentadiene compounds, which are useful for making metallocene catalysts, which are useful for polymerizing olefin monomers such as ethylene, propylene, alpha-olefins, and butadiene to make polyolefin polymers, which have a wide variety of industrial uses.

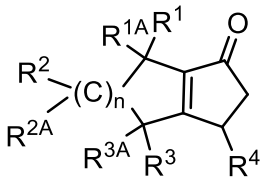
[0008] The present ~~invention~~ disclosure includes a number of ~~embodiments~~examples. A method of synthesizing a substituted cyclopentadiene compound. The synthesis comprises a step of cyclizing, in the presence of a phosphorous pentoxide/methanesulfonic acid reagent (e.g., Eaton's reagent), an alpha,beta-unsaturated carboxylic acid, cycloalkyl ester compound to make a substituted cyclopentenone compound, and converting the substituted cyclopentenone compound to the

substituted cyclopentadiene compound. Also, a method of synthesizing a substituted metallocene compound comprising a metal-(substituted cyclopentadienyl ligand) complex, wherein the substituted cyclopentadienyl ligand is made from the substituted cyclopentadiene compound. A metal-(substituted cyclopentadienyl ligand) complex and substituted metallocene compound made by the method. A substituted metallocene catalyst made from the metal-(substituted cyclopentadienyl ligand) complex or substituted metallocene compound.

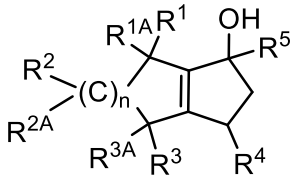
[0008a] In one aspect, the present disclosure refers to a method of synthesizing a substituted cyclopentadiene compound, the method comprising (A) contacting a compound of formula



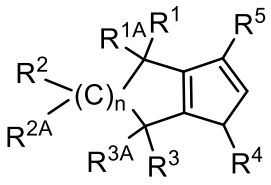
(1) ("compound (1)"): (1), wherein subscript n is 1, 2, 3, or 4; and each of groups R1, R1A, R2, R2A, R3, R3A, and R4 is independently H or (C_1-C_4)alkyl, or any two adjacent R1 to R3 groups, which consist of R1 and R2 or R2 and R3, are bonded together to form a (C_1-C_4)alkylene and the remaining group of R1 to R3 is H or (C_1-C_4)alkyl, with an effective amount of a phosphorous pentoxide/methanesulfonic acid reagent (P_2O_5/H_3CSO_3H reagent) and under reaction conditions sufficient to make a compound of formula (2) ("compound (2)"):

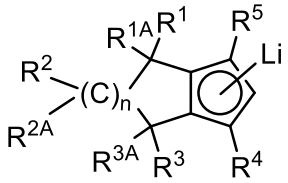
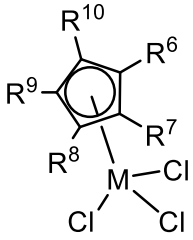
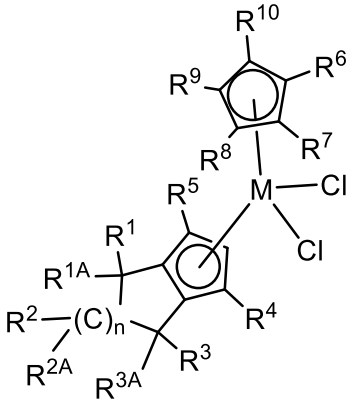


(2); wherein subscript n and groups R1 to R4 are as defined above; and with the proviso that the contacting step (A) is free of a polyphosphoric acid (PPA); (B) contacting the compound (2) with a metal-R5 reducing agent that is either a hydride-functional reducing agent or a (C_1-C_4)alkyl lithium, under reaction conditions sufficient to make a compound of formula (3) ("compound (3)"):



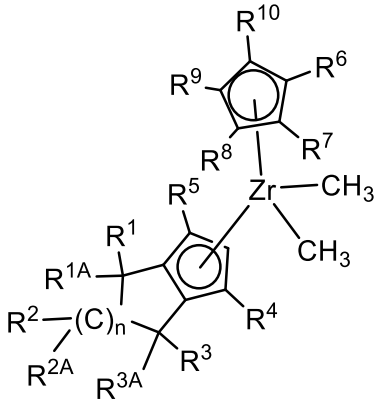
(3), wherein subscript n and groups R1 to R4 are as defined above and R5 is H or (C_1-C_4)alkyl, respectively; and (C) contacting the compound (3) with dehydration reaction conditions to make a substituted cyclopentadiene compound of formula

(4) (“compound (4)”):  (4), wherein subscript n and groups R1-R5 are as defined above.

[0008b] In another aspect, the present disclosure refers to a method of synthesizing a substituted metallocene compound comprising a metal-(substituted cyclopentadienyl ligand) complex, the method comprising synthesizing the compound (4) according to steps (A) to (C) as described herein; (D) contacting the compound (4) with an alkyl lithium under reaction conditions sufficient to make a compound of formula (5) (“compound (5)”):  (5); and (E) contacting the compound (5) with a compound of formula (6) (“compound (6)”):  (6) under reaction conditions sufficient to make a compound of formula (7) (“compound (7)”):  (7) , wherein subscript n and groups R1 to R5 are as defined above; metal M is a metal of Group 4 of the Periodic Table of the Elements; and each of R6 to R8 is independently H or (C_1-C_4)alkyl and R9 and R10 is independently H or (C_1-C_4)alkyl or R9 and R10 are bonded together and are a (C_3-C_5)alkylene.

[0008c] In another aspect, the present disclosure refers to a method of synthesizing a zirconocene dimethyl complex, the method comprising synthesizing the compound (7) according to steps (A) to (E) as described herein, wherein M is Zr; and (F) contacting the

compound (7) with an effective amount of methyl magnesium bromide under reaction conditions sufficient to make a compound of formula (8) ("compound (8)"):



(8), wherein subscript n and groups R1 to R10 are as defined above.

[0008d] In another aspect, the present disclosure refers to a method of polymerizing an olefin, the method comprising synthesizing the compound (7) or synthesizing the compound (8) according to the methods as described herein; contacting the compound (7) or (8) with an activator to make a catalyst; and contacting ethylene and/or an alpha-olefin with the catalyst under conditions sufficient to make a polyolefin polymer comprising a polyethylene homopolymer, an ethylene/alpha-olefin copolymer, or a poly(alpha-olefin) homopolymer; wherein the method is free of platinum, palladium, nickel, rhodium, and ruthenium.

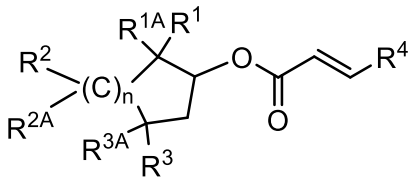
[0009] We discovered a shorter synthesis of substituted cyclopentadiene compounds. The synthesis uses a phosphorous pentoxide/methanesulfonic acid reagent, and may be run at a lower temperature and yet be higher yielding than a prior PPA-based synthesis of Conia et al. Also, the synthesis avoids using a hydrogenation catalyst, a hydrogenation step, and a hydrogenation catalyst filtration step. Therefore, the inventive metal-(substituted cyclopentadienyl ligand) complex and substituted metallocene catalyst made therefrom, and polyolefins made therewith are beneficially free of (added) hydrogenation catalyst metals such as platinum, palladium, nickel, rhodium, and ruthenium. As discussed above, polyolefin degradation problems have been attributed to hydrogenation catalyst metals are reported in the literature, and thus the inventive complex and catalyst beneficially avoid any such problem(s).

DETAILED DESCRIPTION

[0010] The Summary and Abstract are incorporated here by reference.

[0011] Certain inventive embodiments are described below as numbered aspects for easy cross-referencing. Additional embodiments are described elsewhere herein.

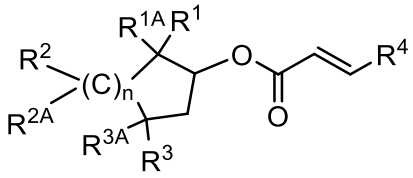
[0012] Aspect 1. A method of synthesizing a substituted cyclopentadiene compound, the method comprising (A) contacting a compound of formula (1) ("compound (1)"):



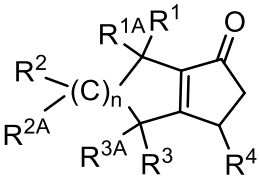
(1), wherein subscript n is 1, 2, 3, or 4; and each of groups R1, R1A, R2, R2A, R3, R3A, and R4 is independently H or (C_1-C_4)alkyl, or any two adjacent R1 to R3 groups are bonded together to form a (C_1-C_4)alkylene and the remaining groups of R1 to R3A is H or (C_1-C_4)alkyl, with an effective amount of a phosphorous pentoxide/methanesulfonic acid reagent (P_2O_5/H_3CSO_3H reagent) and under reaction conditions sufficient to make a compound of formula (2) ("compound (2)"):

CLAIMS

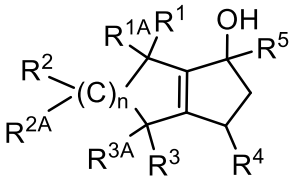
1. A method of synthesizing a substituted cyclopentadiene compound, the method comprising (A) contacting a compound of formula (1) ("compound (1)"):



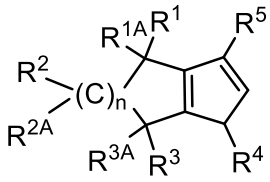
(1), wherein subscript n is 1, 2, 3, or 4; and each of groups R1, R1A, R2, R2A, R3, R3A, and R4 is independently H or (C_1-C_4)alkyl, or any two adjacent R1 to R3 groups, which consist of R1 and R2 or R2 and R3, are bonded together to form a (C_1-C_4)alkylene and the remaining group of R1 to R3~~A~~ is H or (C_1-C_4)alkyl, with an effective amount of a phosphorous pentoxide/methanesulfonic acid reagent (P_2O_5/H_3CSO_3H reagent) and under reaction conditions sufficient to make a compound of formula (2) ("compound (2)"):



(2); wherein subscript n and groups R1 to R4 are as defined above; and with the proviso that the contacting step (A) is free of a polyphosphoric acid (PPA); (B) contacting the compound (2) with a metal-R5 reducing agent that is either a hydride-functional reducing agent or a (C_1-C_4)alkyl lithium, under reaction conditions sufficient to make a compound of formula (3) ("compound (3)"):

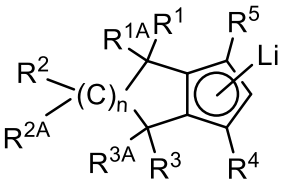
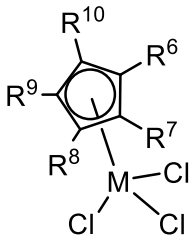
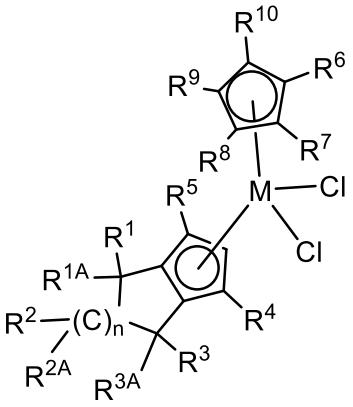


(3), wherein subscript n and groups R1 to R4 are as defined above and R5 is H or (C_1-C_4)alkyl, respectively; and (C) contacting the compound (3) with dehydration reaction conditions to make a substituted cyclopentadiene compound of formula (4) ("compound (4)"):



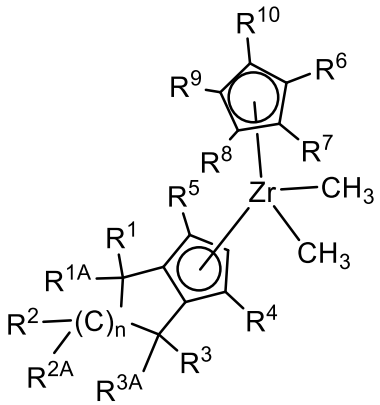
(4), wherein subscript n and groups R1-R5 are as defined above.

2. A method of synthesizing a substituted metallocene compound comprising a metal-(substituted cyclopentadienyl ligand) complex, the method comprising synthesizing the compound (4) according to steps (A) to (C) of claim 1; (D) contacting the compound (4) with an alkyl lithium under reaction conditions sufficient to make a compound of formula (5)

(“compound (5)”):  (5); and (E) contacting the compound (5) with a compound of formula (6) (“compound (6)”):  (6) under reaction conditions sufficient to make a compound of formula (7) (“compound (7)”): 

(7) , wherein subscript n and groups R1 to R5 are as defined above; metal M is a metal of Group 4 of the Periodic Table of the Elements; and each of R6 to R8 is independently H or (C_1-C_4)alkyl and R9 and R10 is independently H or (C_1-C_4)alkyl or R9 and R10 are bonded together and are a (C_3-C_5)alkylene.

3. A method of synthesizing a zirconocene dimethyl complex, the method comprising synthesizing the compound (7) according to steps (A) to (E) of claim 2, wherein M is Zr; and (F) contacting the compound (7) with an effective amount of methyl magnesium bromide under reaction conditions sufficient to make a compound of formula (8) (“compound (8)”):



(8), wherein subscript n and groups R1 to R10 are as defined above.

4. The method of any one of claims 1 to 3, wherein the ratio of P_2O_5 to H_3CSO_3H used to make the P_2O_5/H_3CSO_3H reagent is from 0.05/1 to 1/1 (weight/weight).

5. The method of any one of claims 1 to 4, wherein the ratio of P_2O_5 to H_3CSO_3H used to make the P_2O_5/H_3CSO_3H reagent is 0.1/1 (weight/weight).

6 The method of any one of claims 1 to 5, wherein the compound (4) is selected from the group consisting of any one of compounds (4a) to (4e):

compound (4a) is compound (4) wherein subscript n is 2, R1 to R3A is H and each of R4 and R5 is methyl;

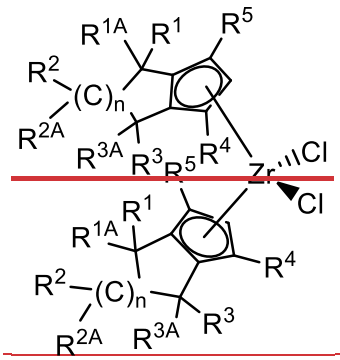
compound (4b) is compound (4) wherein subscript n is 1 and R1-R4 are H and R5 is methyl;

compound (4c) is compound (4) wherein subscript n is 1 and R1-R3A are H and each of R4 and R5 is methyl;

compound (4d) is compound (4) wherein subscript n is 3 and R1-R3A are H and each of R4 and R5 is methyl; and

compound (4e) is compound (4) wherein subscript n is 4 and R1, R1A, two R2, and each R2A are H and two R2 and each of R3, R4 and R5 is methyl.

~~7. A method of making a dichloro compound of formula (9):~~



~~(9) ("compound (9)"), wherein each subscript n independently is 1, 2, 3, or 4; and each of groups R1, R1A, R2, R2A, R3, R3A, R4, and R5 is independently H or (C_1-C_4)alkyl, or any two adjacent R1 to R3 groups are bonded together to form a (C_1-C_4)alkylene and the remaining group of R1 to R5 is H or (C_1-C_4)alkyl, the method comprising contacting two mole equivalents of the compound (5) with one mole equivalent of $ZrCl_4$, under reaction conditions sufficient to make the compound (9).~~

~~8. The method of claim 7 further comprising a step of contacting the compound (9) with an effective amount of methyl magnesium bromide under reaction conditions sufficient to make a dimethyl compound (10) ("compound (10)"), which has a structure identical to that of compound (9) except wherein each Cl atom of compound (i9) is replaced by a methyl group (CH_3) in compound (10).~~

~~9. A compound of formula (9) made by the method of claim 7 or compound (10) made by the method of claim 8.~~

~~10~~7. A method of polymerizing an olefin, the method comprising synthesizing the compound (7) according to the method of claim 2 or synthesizing the compound (8) according to the method of claim 3; contacting the compound (7) or (8) with an activator to make a catalyst; and contacting ethylene and/or an alpha-olefin with the catalyst under conditions sufficient to make a polyolefin polymer comprising a polyethylene homopolymer, an ethylene/alpha-olefin copolymer, or a poly(alpha-olefin) homopolymer; wherein the method is free of platinum, palladium, nickel, rhodium, and ruthenium.

~~11. The polyolefin polymer made by the method of claim 10 and being free of platinum, palladium, nickel, rhodium, and ruthenium.~~