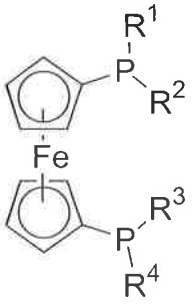
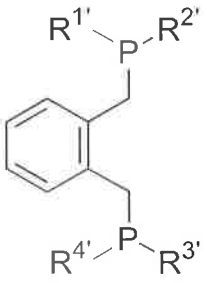
Claims

1. Process comprising the following process steps:
   a) introducing an ethylenically unsaturated compound;
   b) adding a ligand-metal complex comprising Pd and a bidentate phosphine ligand,
      or adding a bidentate phosphine ligand and a compound which comprises Pd;
   c) adding an alcohol;
   d) supplying CO;
   e) heating the reaction mixture, the ethylenically unsaturated compound being reacted to form an ester,

   where the reaction mixture is admixed with less than 0.1 mol%, based on the amount of substance of the ethylenically unsaturated compound, of Brønsted acids having an acid strength of pKa ≤ 5,
   wherein the phosphine ligand is substituted on at least one phosphorus atom by at least one heteroaryl radical, and
   wherein the bidentate phosphine ligand is selected from a compound according to one of the formulae (**I**) and (**II**)



(**I**)



(**II**),

   where
   R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$ are each independently selected from -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl, -(C_3-C_{20})-heteroaryl;
   at least one of the R^1, R^2, R^3, R^4 radicals or at least one of the $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$ radicals is a -(C_3-C_{20})-heteroaryl radical;

and

R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, if they are -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl or -(C_3-C_{20})-heteroaryl,
may each independently be substituted by one or more substituents selected from -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -O-(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl-(C_6-C_{20})-aryl, -O-(C_3-C_{12})-cycloalkyl, -S-(C_1-C_{12})-alkyl, -S-(C_3-C_{12})-cycloalkyl, -COO-(C_1-C_{12})-alkyl, -COO-(C_3-C_{12})-cycloalkyl, -CONH-(C_1-C_{12})-alkyl, -CONH-(C_3-C_{12})-cycloalkyl, -CO-(C_1-C_{12})-alkyl, -CO-(C_3-C_{12})-cycloalkyl, -N-[(C_1-C_{12})-alkyl]$_2$, -(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl-O-(C_1-C_{12})-alkyl, -(C_3-C_{20})-heteroaryl, -(C_3-C_{20})-heteroaryl-(C_1-C_{12})-alkyl, -(C_3-C_{20})-heteroaryl-O-(C_1-C_{12})-alkyl, -COOH, -OH, -SO_3H, -NH_2, halogen.

2. Process according to Claim 1,
where R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$, if they are -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl or -(C_3-C_{20})-heteroaryl,
may each independently be substituted by one or more substituents selected from -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -O-(C_1-C_{12})-alkyl, -O-(C_1-C_{12})-alkyl-(C_6-C_{20})-aryl, -O-(C_3-C_{12})-cycloalkyl, -(C_6-C_{20})-aryl, -(C_6-C_{20})-aryl-(C_1-C_{12})-alkyl, -(C_6-C_{20})-aryl-O-(C_1-C_{12})-alkyl, -(C_3-C_{20})-heteroaryl, -(C_3-C_{20})-heteroaryl-(C_1-C_{12})-alkyl, -(C_3-C_{20})-heteroaryl-O-(C_1-C_{12})-alkyl.

3. Process according to either of Claims 1 and 2,
where R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$ are each independently selected from -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl, -(C_3-C_{20})-heteroaryl;
and at least one of the radicals R^1, R^2, R^3 and R^4, and/or at least one of the radicals $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$, is a -(C_3-C_{20})-heteroaryl radical.

4. Process according to any of Claims 1 to 3,
where at least two of the R^1, R^2, R^3, R^4 radicals or at least two of the $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$ radicals are a -(C_3-C_{20})-heteroaryl radical.

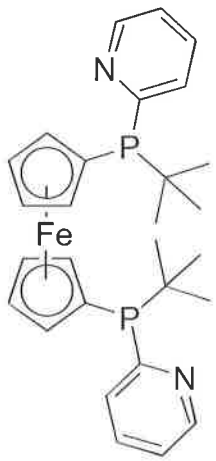
5. Process according to Claim 4,
where the R^1 and R^3 radicals or the $R^{1'}$ and $R^{3'}$ radicals are each a -(C_3-C_{20})-heteroaryl radical.

6. Process according to Claim 5,
where the R^1 and R^3 or $R^{1'}$ and $R^{3'}$ radicals are each a -(C_3-C_{20})-heteroaryl radical; and the R^2 and R^4 or $R^{2'}$ or $R^{4'}$ radicals are each independently selected from -(C_1-C_{12})-alkyl, -(C_3-C_{12})-cycloalkyl, -(C_3-C_{12})-heterocycloalkyl, -(C_6-C_{20})-aryl.

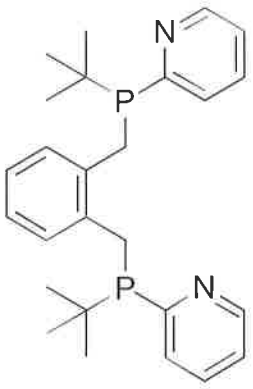
7. Process according to any of Claims 1 to 6,
where the radicals R^1, R^2, R^3 and R^4 and/or $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$, if they are a heteroaryl radical, are a heteroaryl radical having five or six ring atoms.

8. Process according to any of Claims 1 to 7,
where the radicals R^1, R^2, R^3 and R^4 and/or $R^{1'}$, $R^{2'}$, $R^{3'}$ and $R^{4'}$, if they are a heteroaryl radical, are selected from 2-furyl, 2-thienyl, N-methyl-2-pyrrolyl, N-phenyl-2-pyrrolyl, N-(2-methoxyphenyl)-2-pyrrolyl, 2-pyrrolyl, N-methyl-2-imidazolyl, 2-imidazolyl, 2-pyridyl, 2-pyrimidyl, the stated heteroaryl radicals not being further substituted.

9. Process according to Claim 1,
where the bidentate phosphine ligand is selected from a compound according to one of the formulae (**8**) and (**4**)



(**8**)



(**4**).

10. Process according to any of Claims 1 to 9,
wherein the ethylenically unsaturated compound is selected from ethene, propene, 1-butene, *cis*- and/or *trans*-2-butene, isobutene, 1,3-butadiene, 1-pentene, *cis*- and/or *trans*-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, hexene, tetramethylethylene, heptene, 1-octene, 2-octene, di-n-butene, and mixtures thereof.

11. Process according to any of Claims 1 to 10,
wherein the compound comprising Pd in process step b) is selected from palladium dichloride, palladium(II) acetylacetonate, palladium(II) acetate, dichloro(1,5-cyclooctadiene)palladium(II), bis(dibenzylideneacetone)palladium, bis(acetonitrile)dichloropalladium(II), palladium(cinnamyl) dichloride.

12. Process according to any of Claims 1 to 11,
wherein the alcohol in process step c) is selected from methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 2-propanol, *tert*-butanol, 3-pentanol, cyclohexanol, phenol, and mixtures thereof.

13. Process according to any of Claims 1 to 12,
where the reaction mixture is admixed with less than 0.1 mol%, based on the amount of substance of the ethylenically unsaturated compound, of Brønsted acids having an acid strength of pKa ≤ 6.