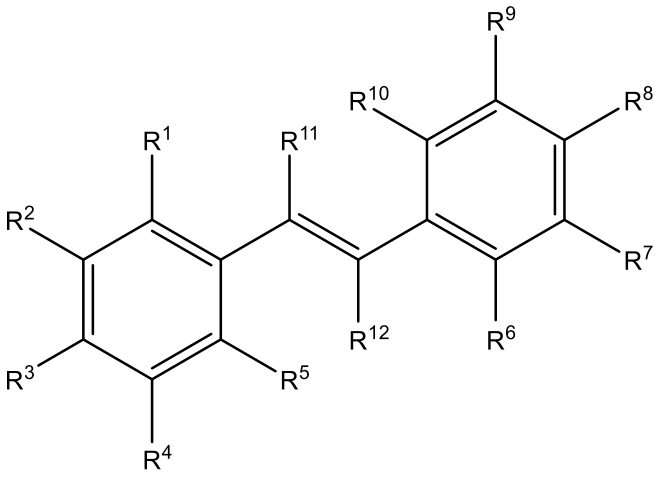
and revealed to be excellent precursors for a wide variety of different Ni-catalyzed reactions.

Summary

The present ~~invention~~ disclosure is therefore directed to $Ni(R)_3$ –complexes wherein Ni represents Ni(0) and R may be the same or different and represents a *trans*-stilbene of the Formula (I):

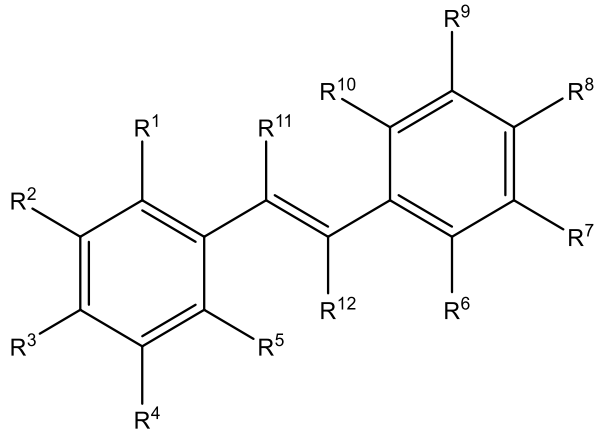


(I)

wherein R^1 to R^{10} may be the same or different and are selected from H, Cl, Br, F, CN, C_1 to C_8 alkyl or C_3 to C_6 cycloalkyl which alkyl or cycloalkyl may optionally be substituted by one or more halogens,
wherein R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_8 alkyl, C^3 to C_6 cycloalkyl, -O-C_1 to C_8 alkyl or -O-C_3 to C_6 cycloalkyl,
with the proviso that at least one of R^1 to R^{12} is not hydrogen.

In the inventive $Ni(R)_3$-complexes as illustrated in the present context, Ni represents Ni(0).

One aspect of the present disclosure refers to an air-stable $Ni(R)_3$ –complex wherein Ni represents Ni(0) and R may be the same or different and represents a trans-stilbene of the Formula (I):



(I)

wherein R^1 to R^{10} may be the same or different and are selected from H, Cl, Br, F, CN, C_1 to C_6 alkyl or C_3 to C_6 cycloalkyl which alkyl or cycloalkyl may optionally be substituted by one or more halogens,
wherein R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_6 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_6 alkyl, or -O-C_3 to C_6 cycloalkyl,
with the proviso that at least one of R^1 to R^{12} is not hydrogen.

In another ~~embodiment~~ example of the inventive $Ni(R)_3$–complex, R is the same or different and in Formula (I), at least one of R^1 to R^5 and at least one of R^6 to R^{10} are the same or different and are selected from Cl, Br, F, CN, C_1 to C_8 alkyl or C_3 to C_6 cycloalkyl which alkyl or cycloalkyl may optionally be substituted by one or more halogens, preferably selected from C_1 to C_8 alkyl which may optionally be branched and/or substituted by one or more halogens, and the others of R^1 to R^{10}

are hydrogen, and R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_8 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_8 alkyl or -O-C_3 to C_6 cycloalkyl .

In yet another example ~~embodiment~~ of the inventive $Ni(R)_3$ –complex, R is the same or different and in Formula (I), R^3 and R^8 are the same or different and are selected from C_1 to C_8 alkyl which alkyl or cycloalkyl may optionally be substituted by one or more halogens, and the others of R^1 to R^{10} are hydrogen, and R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_8 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_8 alkyl or -O-C_3 to C_6 cycloalkyl .

In further example ~~embodiment~~ of the inventive $Ni(R)_3$ –complex, R is the same or different and in Formula (I), R^3 and R^8 are the same or different and are selected from branched C_3 to C_8 alkyl such as isopropyl, t-butyl, neopentyl, which may optionally be substituted by one or more halogens, and the others of R^1 to R^{10} are hydrogen, and R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_8 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_8 alkyl or -O-C_3 to C_6 cycloalkyl .

In a yet further example ~~embodiment~~ of the inventive $Ni(R)_3$ –complex, R is the same and in Formula (I), R^3 and R^8 are the same or different and are selected from C_1 to C_8 perfluoroalkyl and the others of R^1 to R^{10} are hydrogen, and R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_8 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_8 alkyl or -O-C_3 to C_6 cycloalkyl.

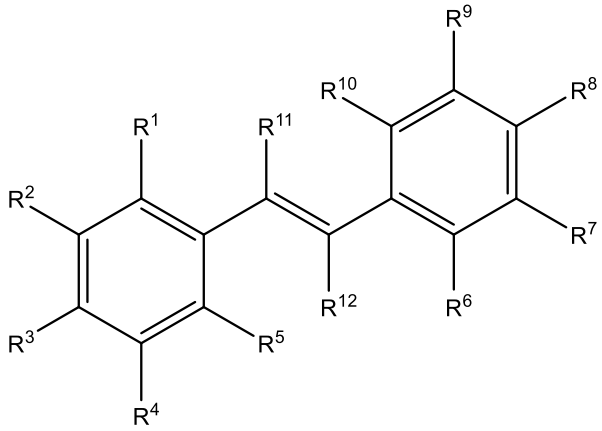
In yet another example ~~embodiment~~ of the inventive $Ni(R)_3$ –complex, R is the same and in Formula (I), R^3 and R^8 are each C_1 to C_8 perfluoroalkyl, preferably CF_3, and the others of R^1 to R^{10} and R^{11} to R^{12} are hydrogen.

In the ~~invention~~disclosure, alkyl is intended to represent any alkyl group having one to eight carbon atoms including branched alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, t-butyl, pentyl, neopentyl, iso-pentyl, hexyl, iso-hexyl, heptyl, iso-heptyl, octyl, iso-octyl.

In the disclosure~~invention~~, cycloalkyl is intended to represent any cycloalkyl group having three to six carbon atoms including alkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and substituted alkyl rings.

Every alkyl or cycloalkyl group may be substituted by one or more halogens, particularly by fluorine.

Another aspect of ~~The~~the present ~~invention~~ disclosure~~also~~ refers to a process for preparing an ~~the inventive~~ air-stable $Ni(R)_3$ –complex~~es~~ wherein Ni represents Ni(0) and R may be the same or different and represents a *trans*-stilbene of the Formula (I):



(I)

wherein R^1 to R^{10} may be the same or different and are selected from H, Cl, Br, F, CN, C_1 to C_6 alkyl or C_3 to C_6 cycloalkyl which alkyl or cycloalkyl may optionally be substituted by one or more halogens,
wherein R^{11} to R^{12} may be the same or different and are selected from H, C_1 to C_6 alkyl, C_3 to C_6 cycloalkyl, -O-C_1 to C_6 alkyl, or -O-C_3 to C_6 cycloalkyl,
wherein Nickel (II) compound, selected from NiF_2, $NiCl_2$, $NiBr_2$, NiI_2, $Ni(OTf)_2$, $Ni(BF_4)_2$, $Ni(OTs)_2$, $Ni(glyme)Cl_2$, $Ni(glyme)Br_2$, $Ni(diglyme)Cl_2$, $Ni(diglyme)Br_2$, $Ni(NO_3)_2$, $Ni(OR^{13})_2$ (where R^{13} represents -C(O)-C_1-C_6-alkyl which is optionally substituted with one or more halogen, preferably Cl or F, Ni(acetyl acetonate)$_2$, $Ni(Ac)_2$ or mixtures thereof, is reacted with the *trans*-stilbene of Formula (I), preferably at least three equivalents, in the presence of an aluminum alkyl of the Formula $Al(R^{14})_3$, preferably at least two equivalents, wherein R^{14} may be the same of different and is selected from C_1 to C_6 alkyl or C_3 to C_6 cycloalkyl.

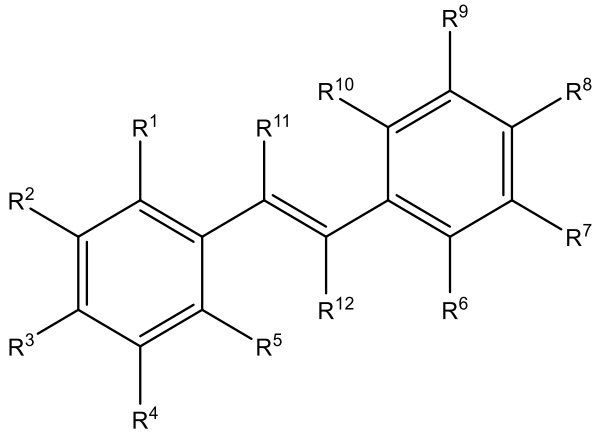
In an example ~~embodiment~~ of the inventive process for preparing air-stable $Ni(R)_3$ –complexes as detailed before, the aluminum alkyl of the Formula $Al(R^{14})_3$ is selected from $Al(CH_3)_3$ or $Al(C_2H_5)_3$.

In yet another example ~~embodiment~~ of the inventive process for preparing air-stable $Ni(R)_3$ –complexes as detailed before, R represents a *trans*-stilbene of the Formula (I) as defined in any of claims 2 to 5.

In another example ~~embodiment~~ of the inventive process, the *trans*-stilbene of Formula (I) is used wherein at least one of R^1 to R^{12} is not hydrogen.

In the inventive process, the choice of the solvent is not critical as long as the solvent is an aprotic non-polar organic solvent selected from diethylether, aromatic solvents such as benzene, toluene, aliphatic hydrocarbon solvents having 5 to 8 carbon atoms, such as pentane, hexane, or mixtures thereof. The reaction conditions are also not critical and the reaction is usually carried out at a temperature between -78°C to 0°C, preferably -30° to -5°C, under ambient pressure and optionally under an inert gas atmosphere. The reaction is usually carried out with a slight stoichiometric excess of the *trans*-stilbene of Formula (I), preferably at least three equivalents, and of the aluminum alkyl of the Formula $Al(R^{14})_3$, preferably at least two equivalents, each of the *trans*-stilbene of Formula (I) and of the aluminum alkyl of the Formula $Al(R^{14})_3$ preferably up to additional 10 mol %.

Another aspect of the present disclosure refers to a use of an air-stable $Ni(R)_3$ –complex as defined herein as catalyst or precatalyst in organic synthesis, wherein: Ni represents Ni(0) and R may be the same or different and represents a *trans*-stilbene of the Formula (I):



(I)

R^1 to R^{10} may be the same or different and are selected from H, Cl, Br, F, CN, C_1 to C_6 alkyl or C_3 to C_6 cycloalkyl which may optionally be substituted by one or more halogens,

R^{11} to R^{12} may be the same or different and are selected from H, -O-C_1 to C_6 alkyl, C_1 to C_6 alkyl or C_3 to C_6 cycloalkyl,

optionally with the proviso that at least one of R^1 to R^{12} is not hydrogen.

Another aspect of the~~The~~ present disclosure ~~invention also~~ refers to the use of an ~~the inventive~~ air-stable $Ni(R)_3$–complex~~es~~ as catalyst~~s~~ in organic synthesis.~~,~~ ~~wherein~~ Here, Ni represents Ni(0) and R may be the same or different and represents a *trans*-stilbene of the Formula (I):