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(54) Title: RUTHENIUM AND OSMIUM METAL CARBENE COMPLEXES FOR OLEFIN METATHESIS POLYMERIZATION

(57) Abstract

Processes for the synthesis of several new carbene compounds of ruthenium and osmium are provided. These novel complexes function as stable, well-defined catalysts for the metathesis polymerisation of cyclic olefins.

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TITLE

RUTHENIUM AND OSMIUM METAL CARBENE COMPLEXES FOR OLEFIN METATHESIS POLYMERIZATION

BACKGROUND OF THE INVENTION

This invention relates to new ruthenium and osmium metal carbene complex compounds and their utility in an improved catalytic process for olefin metathesis polymerization.

During the past two decades, research efforts have enabled an in depth understanding of the olefin metathesis reaction as catalyzed by early transition metal complexes. In contrast, the nature of the intermediates and the reaction mechanism for Group VIII transition metal catalysts has remained elusive. In particular, the oxidation states and ligation of the ruthenium and osmium metathesis intermediates are not known. Furthermore, the discrete ruthenium and osmium carbene complexes isolated to date do not exhibit metathesis activity.

Many ruthenium and osmium metal carbenes have been reported in the literature (for example, see Burrell, A. K., Clark, G. R., Rickard, C. E. F., Roper, W. R., Wright, A. H., *J. Chem. Soc.*, Dalton Trans., 1991, Issue 1, pp. 609-614).

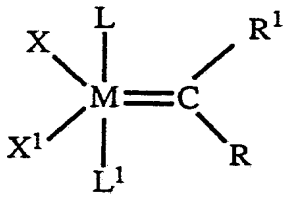
SUMMARY OF THE INVENTION

The present invention involves a reaction of a ruthenium or osmium compound with either a cyclopropene or a phosphorane to produce well-defined carbene compounds which can be called carbene complexes and which can catalyze the polymerization of cyclic olefin via ring-opening metathesis.

The carbene compounds of the present invention are the only Ru and Os carbene complexes known to date in which the metal is formally in the +2 oxidation state,

has an electron count of 16, and is pentacoordinate. The compounds claimed herein are active catalysts for ring-opening metathesis polymerization ("ROMP"). Most metathesis catalysts presently known are poisoned by functional groups and are, therefore, incapable of catalyzing metathesis polymerization reactions in protic or aqueous solvent systems.

Thus, the present invention pertains to compounds of the formula



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wherein:

M is Os or Ru;

R and R^1 are independently selected from hydrogen; C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20} alkynyloxy, aryloxy, C_2-C_{20} alkoxycarbonyl, C_1-C_{20} alkylthio, C_1-C_{20} alkylsulfonyl or C_1-C_{20} alkylsulfinyl; each optionally substituted with C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy or with a phenyl group optionally substituted with halogen, C_1-C_5 alkyl or C_1-C_5 alkoxy;

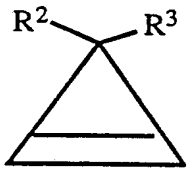
X and X^1 are independently selected from any anionic ligand; and

L and L^1 are independently selected from any neutral electron donor.

In one embodiment of these compounds, they can be in the form wherein 2, 3, or 4 of the moieties X, X^1, L, and L^1 can be taken together to form a chelating multidentate ligand. In one aspect of this embodiment,

X, L, and L^1 can be taken together to form a cyclopentadienyl, indenyl, or fluorenyl moiety.

The present invention also pertains to a method of preparing the aforementioned ruthenium and osmium compounds comprising reacting a compound of the formula $(XX^1ML_nL^1_m)_p$, in the presence of solvent, with a cyclopropene of the formula



wherein:

M, X, X^1, L, and L^1 have the same meaning as indicated above;

n and m are independently 0-4, provided n+m=2, 3 or 4;

p is an integer equal to or greater than 1; and

R^2 and R^3 are independently selected from hydrogen; C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_2-C_{18} alkynyl, C_2-C_{18} alkoxycarbonyl, aryl, C_1-C_{18} carboxylate, C_1-C_{18} alkenyloxy, C_2-C_{18} alkynyloxy, C_1-C_{18} alkoxy, aryloxy, C_1-C_{18} alkylthio, C_1-C_{18} alkylsulfonyl or C_1-C_{18} alkylsulfinyl; each optionally substituted with C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy or with a phenyl group optionally substituted with halogen, C_1-C_5 alkyl or C_1-C_5 alkoxy.

In one embodiment of the process, X, L, and L^1 are taken together to form a moiety selected from the group consisting of cyclopentadienyl, indenyl or fluorenyl, each optionally substituted with hydrogen; C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20}

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