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Review

Agostic bonds in cyclometalation

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ABSTRACT

Cyclometalation reactions proceed very easily with one step reaction between metal compounds and substrates having a heteroatom such as O, S, N, P and As. However, under mild reaction conditions, many agostic compounds which are intermediates in these cyclometalation reactions, can be isolated. The metal compounds used for the formation of these agostic intermediates are both transition metal and main group metal compounds. The substrates are nitrogen-containing compounds, phosphorus-containing compounds, oxygen-containing compounds and sulfur-containing compounds. These agostic intermediates are mainly δ-C–H agostic compounds, some are γ-C–H agostic compounds and very few are ε-C–H-agostic compounds. The agostic intermediates are prepared, usually, under mild reaction conditions in the cyclometalation reaction. These agostic compounds are also prepared from cyclometalation reaction products, e.g., by the protonation, irradiation, and elimination of ligand molecules by vacuum, inert gas current, dehydration with a molecular sieves 4A, etc. Some agostic compounds are utilized for preparation of stable catalysts, e.g., hydrogenation catalysts.

Contents

1. Introduction

Organometallic intramolecular-coordination compounds, mainly, five-membered ring compounds, are synthesized by the cyclometalation reactions as shown in Eq. (1). The cyclometalation reactions proceed very easily, and an enormous amount of cyclic compounds have been synthesized not only with transition metal

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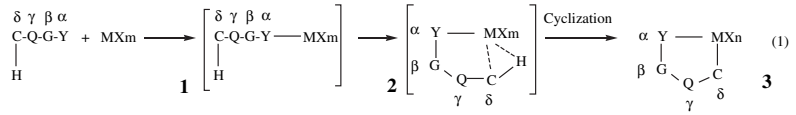
Cyclometalation



MXm, MXn = metal compounds
M = transition metals and main group metals:
68 kinds of metals
Y = N, P, O, S, etc.
G, Q = C, Y

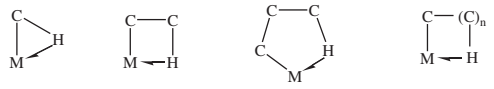
compounds, but also with main group metal compounds. The number of articles on the cyclometalation reactions has increased dramatically since 1970s, and also reviews [1–22] and a book [23] have been published. The number of the metal element in the organometallic intramolecular-coordination compounds, which are synthesized by these cyclometalation reactions was 57 in 2004 [21], 68 in 2007 [22], and 69 in 2010 [24].

In the Cambridge Structural Database of X-ray and neutron diffraction analyses of carbon-containing molecules in a recent listing, the number of the five-membered ring compounds (the heteroatom is N, P, O and S) with the transition metal compounds is 8466 and 2325 with main group metal compounds (group 1, 2, 12, 13, Si, Ge, Pb, As, Sb, Bi, Se and Te).

Almost all kinds of metal compounds are used for these reactions, because these cyclometalation reactions proceed very easily.

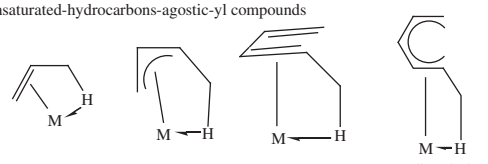
Table 1
Classification of agostic bonds [25].

1. Agostic alkyl compounds



2. Agostic alkylidene compounds
(Agostic carbene compounds)

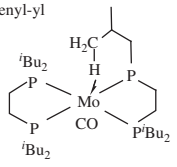
3. Unsaturated-hydrocarbons-agostic-yl compounds



4. Other agostic compounds

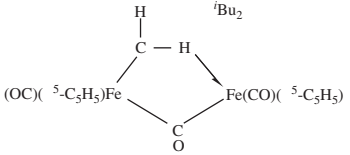
4.1 Remote M–H –C bonds

Example :



4.2 Polynuclear agostic compounds

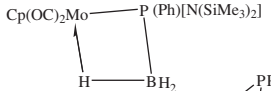
Example :



5. Bridged compounds

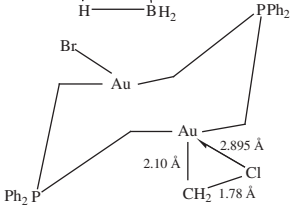
5.1 Hydrogen bridged compounds
(Metal–H–Z ; Z = B, N,Si, Cl, F)

Example : Metal-Hydrogen-Boron Bridge



5.2 Other bridged compounds

Example : Gold-Halogen-Carbon Bridge



Hence the cyclometalations are utilized for organic syntheses, and the cyclometalation products are utilized as catalysts as described in the previous review [22].

Recently, many articles on agostic interactions reported these reaction intermediates prepared under mild reaction conditions in cyclometalation reactions or the derivatives of the reaction products.

This review summarizes the role of agostic compounds in the cyclometalation reactions.

2. Agostic bonds

The term agostic is used to discuss the various manifestations of covalent interactions between, mainly, carbon–hydrogen groups and transition metal centers in organometallic compounds, in which a hydrogen atom is covalently bonded simultaneously with both a carbon atom and a transition metal atom [25–27].

The classification of compounds with agostic bonds are shown in Table 1 [25].

Noticeable tendencies in the formation of agostic bonds shown in Table 2 [25–28].

Certain M···H–C interactions are not classified as “agostic” but are described by a term “hydrogen bonding (anagostic

Table 2
Noticeable tendencies in the formation of agostic bonds [25–28].

1. Substrates
Compounds having a heteroatom such as N, P, O and S, and having a δ-C–H bond
2. Metal atom:
a) Mainly transition metal atoms such as Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt.
b) Rarely, 1. 2. and 3 groups’ metal atoms such as Li, Na, Ca, Sr.
c) Coordinatively unsaturated metals such as 14 and 16 electrons.
3. Reactions
a) Low energy, 8–18 kcal mol^{-1}.
b) Reaction conditions are mild, at room temperature, or low temperature.
c) Proton acceptors accelerate the reactions.
For example, AcO^- and OR^-.
d) Irradiation with ultraviolet light
4. Form new reaction sites
a) Eliminate hydrogen atom, hydrogen molecules, solvents, by vacuum or by flowing intergas such as argon.
b) Reaction with bases such as amines and sodium salts.
5. Agostic bonds
a) All agostic bonds are bent, 90–130°.
b) The agostic C–H distances is in the range of 1.13–1.19 Å and is elongated 5–10% relative a no bridging C–H bond.
c) The M–H distances in M ← H–C bonds are also substantially longer (10–20%) than expected for a normal terminal M–H bond.
d) These effects can clearly be ascribed to the presence of a three-center, two-electron M ← H–C bond with the consequent reduction of the C–H and M–H bond orders (2e–3c).
6. Analysis
a) The most useful spectroscopic technique for detecting the presence of agostic systems in compounds is NMR spectroscopy. The agostic is J(C–H) is 60–90 Hz.
b) IR spectroscopy. In all cases, the bands assignable to γ-C–H are found at lower frequencies than for normal sp^3-CH band and occurring the range 2250–2800 cm^{-1}.