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Review

Thermal studies on metallacycloalkanes

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Contents

Abstract

This review describes thermal decomposition studies that have been carried out on metallacycloalkane compounds, and also includes discussion on reaction mechanisms. The decomposition pathways for these compounds are strongly dependent on the nature of the metal, the ligand system, as well as solvent and temperature. The organic product distribution on the decomposition of metallacycloalkanes is also discussed.

Keywords: Metallacycloalkane compounds; Thermal decomposition studies; Product analysis; Decomposition mechanism; Ethylene oligomerisation; 1-Alkene

1. Introduction

Organometallic compounds are in some cases unstable because of the presence of reactive metal–carbon bonds and on thermolysis, give interesting organic products [1,2]. Also, attention has been recently focussed on the pyrolysis studies of organometallic precursors, which have potential applications in the preparation of multi-walled as well as single-walled carbon nanotubes [3,4] and a wide range of inorganic materials as thin films on a variety of substances [5,6]. Metallacycloalkane compounds are an important class of organometallic compounds,

Abbreviations: bipy, 2,2′-bipyridine; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; PCy_3, tricyclohexylphosphine; $PCyp_3$, tricyclopentylphosphine; dpe, (diphenylphosphino)ethane; dppe, 1,2-bis (diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dmpe, 1,2-bis(dimethylphosphino)ethane; dcpe, 1,2-bis(dicyclohexylphosphino) ethane; P^iPr_3, tri-isopropylphosphine; P^tBu_3, tri-*tert*-butylphosphine; Pde, phosphodiesterase; PEt_3, triethylphosphine; PMe_3, trimethylphosphine; tmen, tetramethylethylenediamine

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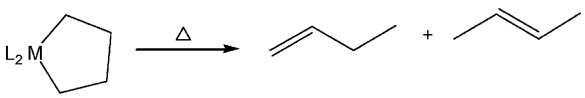
which are known to be key intermediates in olefin metathesis, hydrocarbon cracking and isomerization, epoxidation, de-epoxidation and oligomerisation of alkenes [7,8]. The chemistry of metallacycloalkane compounds is a growing area of organometallic chemistry [8]. These compounds also play an important role in many catalytic transformations. Thus, metallacyclopentanes appear to be key intermediates in a number of olefin dimerization reactions [7,9]. Ethylene trimerisation, tetramerisation and oligomerisation to high linear α-olefins proceed by the intermediacy of metallacycloheptanes, metallacyclononanes and larger size rings [10]. Recently, certain platinacyclobutanes with attached biomolecules have been used as targeted, cisplatin prodrugs [11].

There are only a few review articles on metallacycloalkanes reported in the literature and in these, thermal decomposition studies are restricted to small and medium ring size metallacycloalkanes [8,12–14]. A recent review published in 1999 includes decomposition studies of group 10 metallacycles [12].

The purpose of this present article is to assess the stability of the wide range of known metallacycloalkanes at various temperatures and to discuss the range of interesting organic products produced upon their decomposition. We also include some of our recent results on the thermal decomposition studies of various metallacycloalkanes [15,16]. This article brings together the extensive research on the thermolysis reactions of metallacycloalkanes, particularly focusing on the organic product formation.

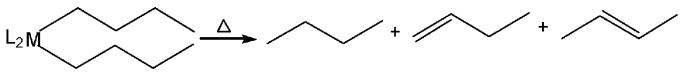
Decomposition to organic products is the termination step in the mechanism of every synthetically useful catalytic or stoichiometric reaction in which a metallacycle is involved [12]. Therefore, studies on the decomposition behaviour of organometallic compounds are fundamental to the development of organometallic chemistry and provide a better understanding of the role of organometallic complexes in organic synthesis and catalysis [13].

Metallacycloalkanes have two metal–carbon single bonds and can formally be regarded as metal complexes with two alkyl ligands; however, their chemistry can be quite different from that of acyclic dialkyl complexes [13]. Based on the thermal decomposition studies, metallacyclobutanes, -pentanes and -hexanes which have quite rigid rings are found to be much more thermally stable than their acyclic analogues. For instance, Whitesides and co-workers [17,18] studied the decomposition of five-membered platinum metallacycles **1a** and **1b** in CH_2Cl_2 at 120 °C while the related acyclic dialkyl complexes (**2a**, **2b**) decomposed at 60 °C in the same solvent. Similarly, the palladacyclopentane **1c** [19] decomposes slowly in toluene at 95 °C (ca. 12 h) while the dibutyl palladium complex **2c** requires only 1 h for complete decomposition at the same temperature.



1a, M = Pt, L = PPh_3
1b, M = Pt, L_2 = dppe
1c, M = Pd, L_2 = dppe

(1)



2a, M = Pt, L = PPh_3
2b, M = Pt, L_2 = dppe
2c, M = Pd, L_2 = dppe

(2)

In contrast, and from limited studies, it appears that the conformationally flexible larger size rings have lower thermal stability [17,18,20] and the chemistry of these compounds has been said to become increasingly indistinguishable from that of dialkyl compounds [13].

The most important application of metallacycloalkanes is in affording linear α-olefins by decomposition of catalytic intermediates in ethylene oligomerisation. Linear α-olefins are useful and widely used in the chemical industry [21].

According to the reported literature, selective catalytic ethylene trimerisations to 1-hexene are based on chromium, tantalum and titanium as well as zirconium and vanadium [21]. Tetramerisation of ethylene, involves the insertion of an ethylene molecule into a metallacycloheptane to form a metallacyclononane, which then decomposes to give 1-octene. The first catalyst capable of ethylene tetramerisation with selectivities of up to 70% 1-octene was reported recently [22,23]. In addition, Tomov et al. [10] provided experimental evidence for the presence of large ring metallacyclic intermediates in catalytic reactions that give higher ethylene oligomers using homogeneous chromium catalysts. Various theoretical studies on titanium- [24,25], tantalum- [26], zirconium- and hafnium-based [27] selective ethylene oligomerisation catalysts have also been reported recently. The catalytic cycle and proposed mechanistic pathway based on chromium is shown in Scheme 1.

2. Decomposition pathways for metallacycloalkanes

The decomposition pathways of metallacycloalkanes may be the termination step in several important catalytic processes [7]. The thermal chemistry of metallacycloalkanes involves several known processes including β-hydride elimination, reductive elimination, α-hydride elimination and carbon–carbon bond cleavage (Fig. 1) [12], as well as certain specific processes which have only been proposed in metallacyclic systems.

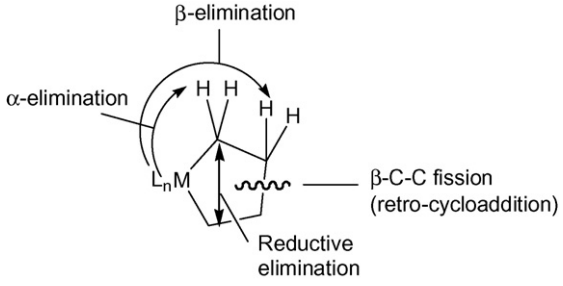
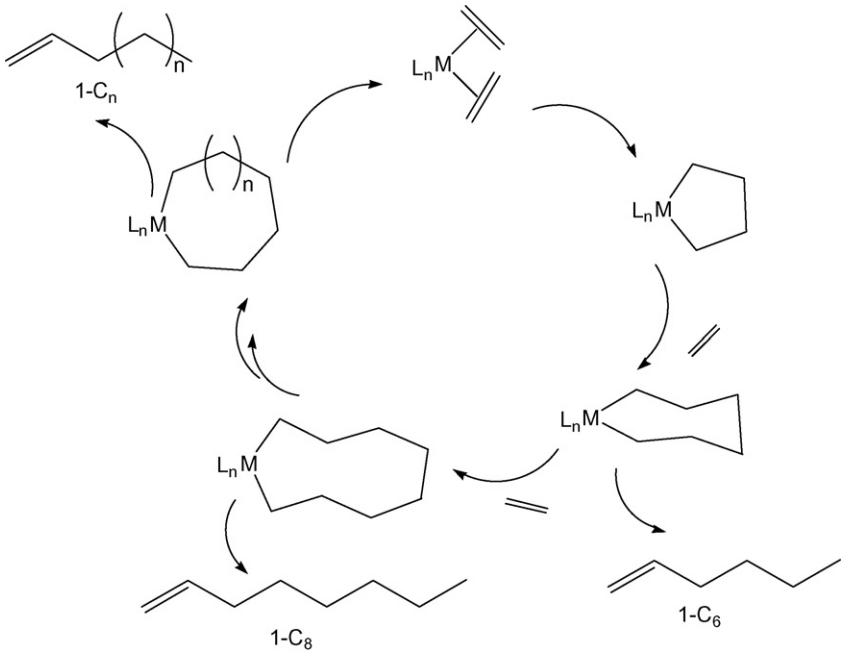


Fig. 1. The conventional decomposition pathways for metallacycloalkanes.

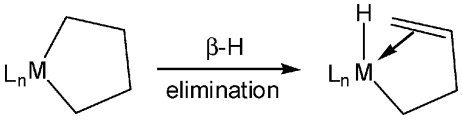


Scheme 1. Catalytic cycle for ethylene trimerisation, tetramerisation and polymerisation.

2.1. β-Hydride elimination

β-Hydride elimination probably occurs most readily from conformations of the organometallic compounds in which M–C–C–H dihedral angles are 0° [17]. This is the most common decomposition pathway for acylic transition metal alkyls, however, it is more hindered in six-, five-, four-, (and three-) membered metallacycles since their M–C–C–H dihedral angles would be greater than 90° [17,18].

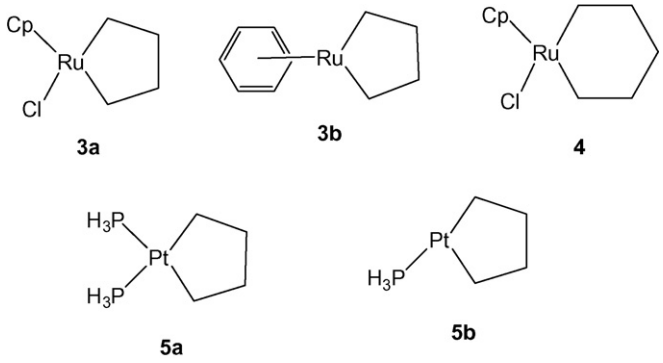
In fact, no metallacyclobutane has ever been directly observed to form an allyl hydride complex by β-hydride elimination [13]. However, β-hydride elimination reactions of five-membered metallacyclic complexes, to give hydridometal alkene complexes (Eq. (3)), are thought to be possible according to recent evidence [25–27].



(3)

To explore this possibility, Huang et al. [28] carried out systematic theoretical calculations to study the β-hydride elimination in several metallacyclic complexes of ruthenium and platinum shown in Scheme 2. It was found that favourable structural arrangements, in which the transferring β-hydrogen is in close proximity to the metal center, for β-hydride elimination exist in 16-electron ruthenacyclopentanes (**3a**, **3b**) and -hexanes (**4**). In contrast, the corresponding reactions of platinum complexes (**5a**, **5b**) appeared more difficult.

In seven-membered and larger metallacycloalkanes, β-hydride elimination is expected to be less hindered [18].



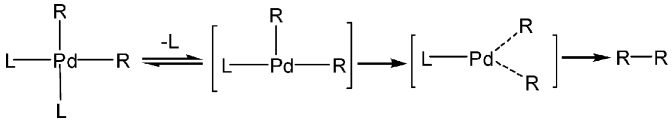
Scheme 2. Metallacyclic species of ruthenium and platinum.

2.2. Reductive elimination

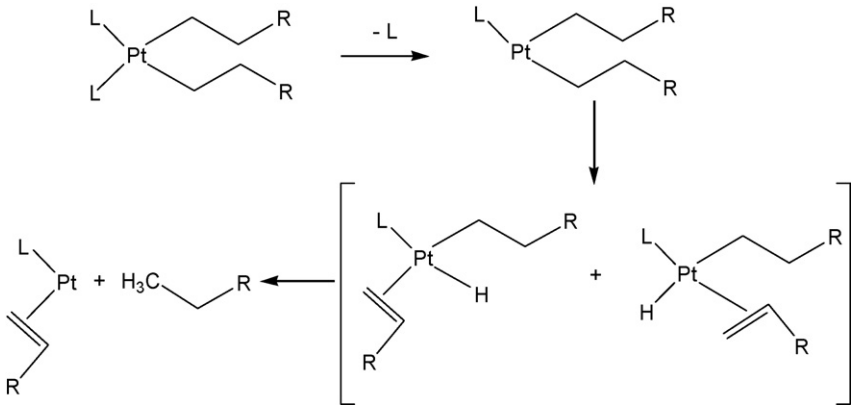
Carbon–carbon bond formation by reductive elimination from transition metal alkyls is an important product forming reaction in organometallic synthesis and catalysis [29].

This process is frequently observed in dialkyls. Thus in complexes such as PtR_2L_2 (L = PPh_3, R = alkyl), reductive elimination of a C–H bond to form alkane from an intermediate hydridoalkylplatinum(II) is the major step when decomposing (Scheme 3) [18].

In contrast, *cis*-PdR_2L_2 compounds afford C–C bond reductive elimination products exclusively [30] (Eq. (4)), while the *trans*-isomers give β-hydride elimination products.

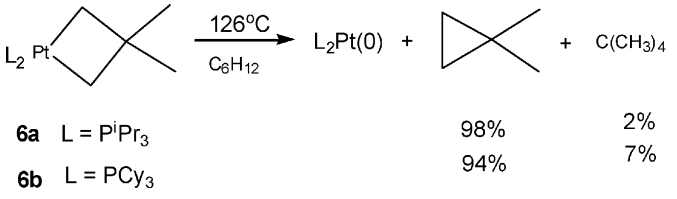


(4)



Scheme 3.

Reductive elimination of a C–C bond to form cycloalkanes is also an important decomposition pathway for some metallacycloalkanes. A typical example of such a process is seen in the decomposition of bis(trialkylphosphane)-3,3-dimethyplatinacyclobutanes **6a** and **6b**, for which there was no β-elimination possible; this was demonstrated some years ago by DiCosimo and Whitesides [31]:

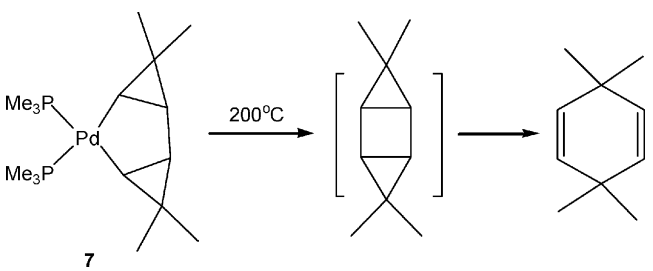


6a L = P^iPr_3 98% 2%

6b L = PCy_3 94% 7%

(5)

In some metallacycles which have a rigid carbon skeleton, the most common decomposition pathway is reductive elimination accompanied by some type of rearrangement. As an example, the palladacyclopentane **7** with the extremely rigid ring decomposes by reductive elimination followed by rearrangement (Eq. (6)) [32], while the nickelacyclopentane **8** experiences rearrangement and a ring expansion, prior to reductive elimination [33]:



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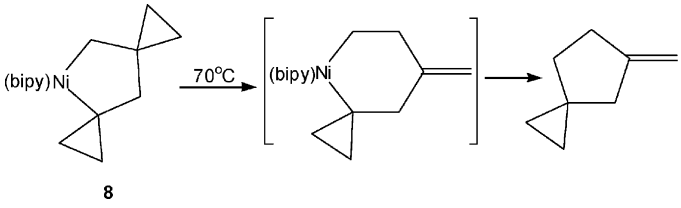
(6)

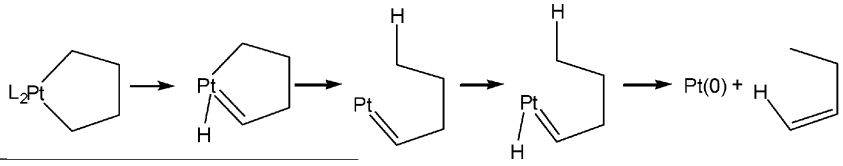


8

(7)

2.3. α-Hydride elimination

Hydride elimination from the α-position, that is, from the carbon directly bonded to the metal, is much less favourable than that from the β carbon. The possibility of an olefin extrusion step starting with α-hydride elimination (Eq. (8)) was suggested in the decomposition mechanisms of the platinacyclopentane compound **1a** by Whitesides and co-workers [18].

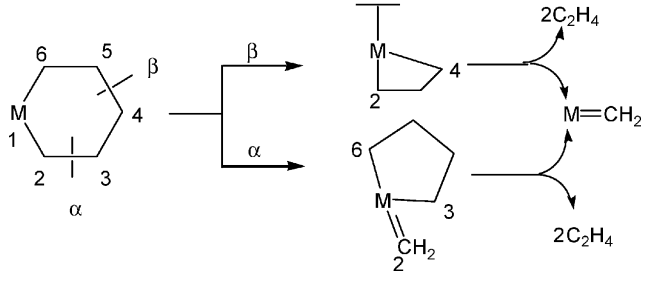


(8)

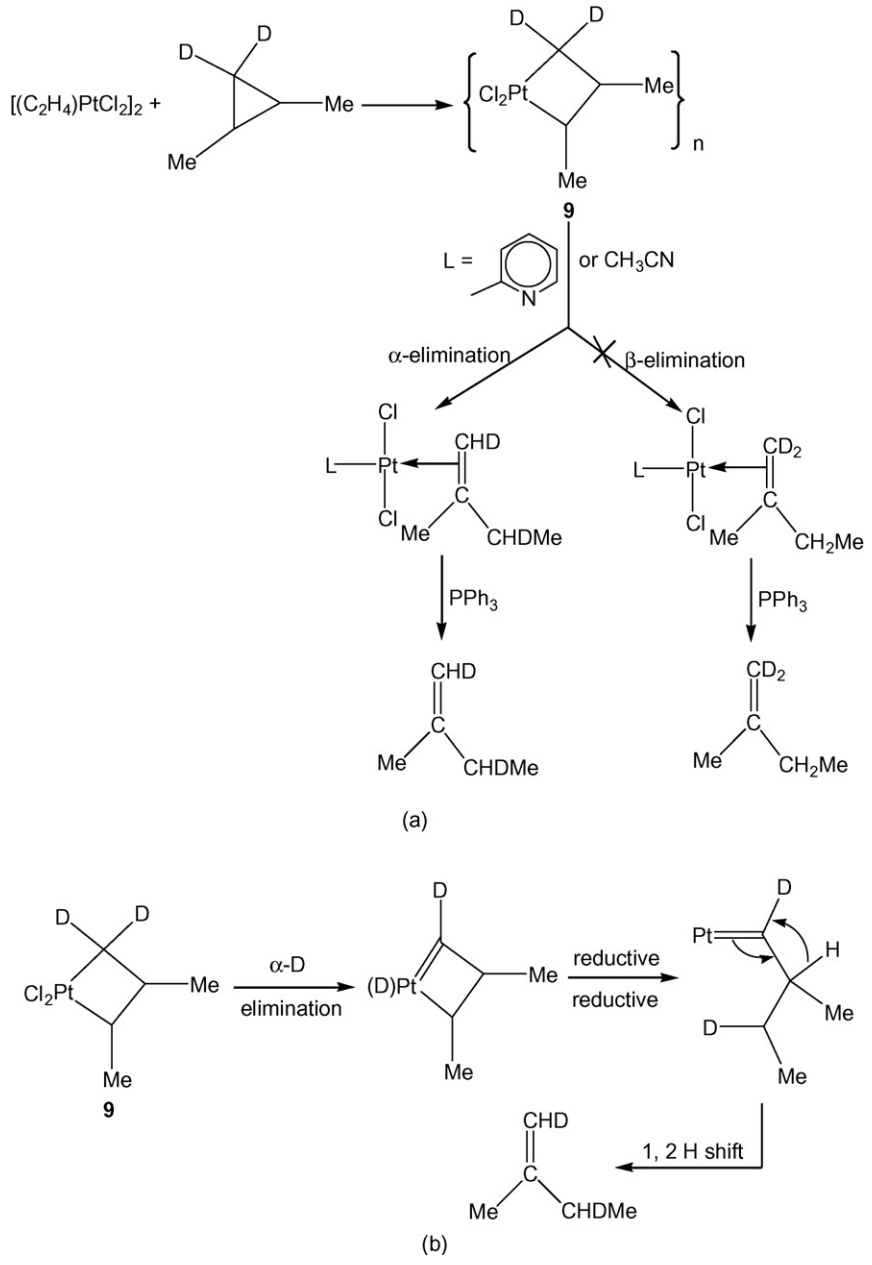
The rearrangement of platinacyclobutane **9** was initially studied by Burton and Puddephatt [34], and the reaction mechanism was later reported by Fischer et al., who provided evidence for the α-hydride elimination step [35] (Scheme 4).

2.4. Carbon–carbon bond cleavage

α- or β-Carbon–carbon bond cleavage (retro-cycloaddition) can be a facile process in simple organometallic complexes [9]:

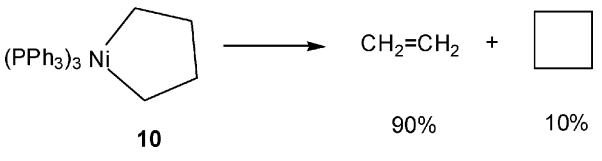


(9)



Scheme 4.

β-Carbon–carbon bond cleavage, expected to be the major pathway of decomposition of metal alkyls, always takes place in metallacyclopentane systems that have symmetrical, β, β-carbons. Decomposition of the five-coordinate nickelacyclopentane **10** [36] and titanacyclopentane **11** [37] to produce ethylene are typical examples:



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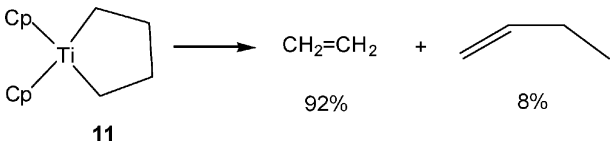
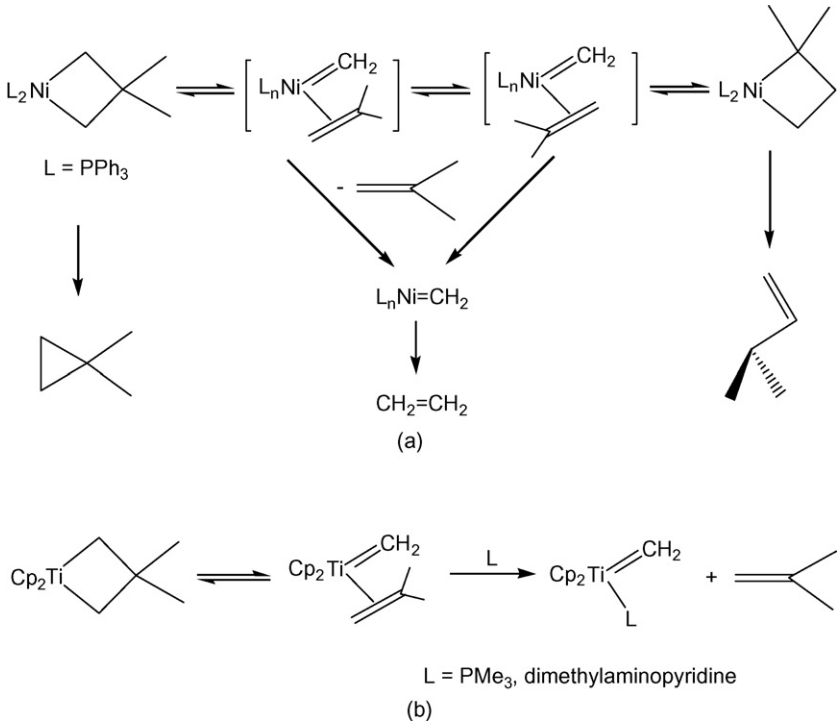
(10)



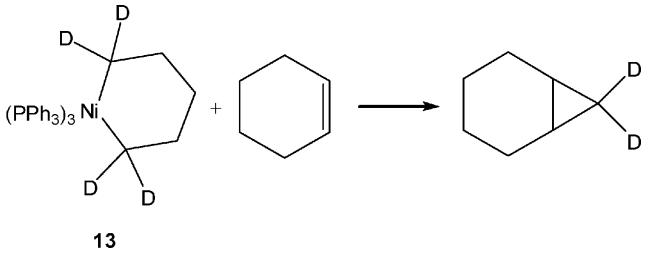
11

(11)

However, the evidence for the formation of a metal carbene intermediate by α-carbon–carbon bond cleavage is very strong in Ni [38] and Ti [39,40] systems (Scheme 5). The α-cleavage seems to be the major route in decomposition of nickelacyclohexane **12** in the presence of cyclohexene (Scheme 6), which was also demonstrated by partially deuterated metallacyclic complex **13** [9,14(a)]:

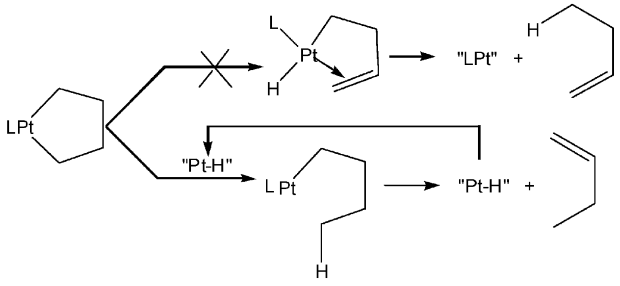


Scheme 5.



(12)

bis(tricyclopentylphosphine)platinacyclopentane [41]. In this work, the authors suggested that the decomposition pathway is an intermolecular hydride chain transfer process, and not the simple β-hydride elimination/reductive elimination pathway, due to the high thermal stability of the platinacyclopentane ring:

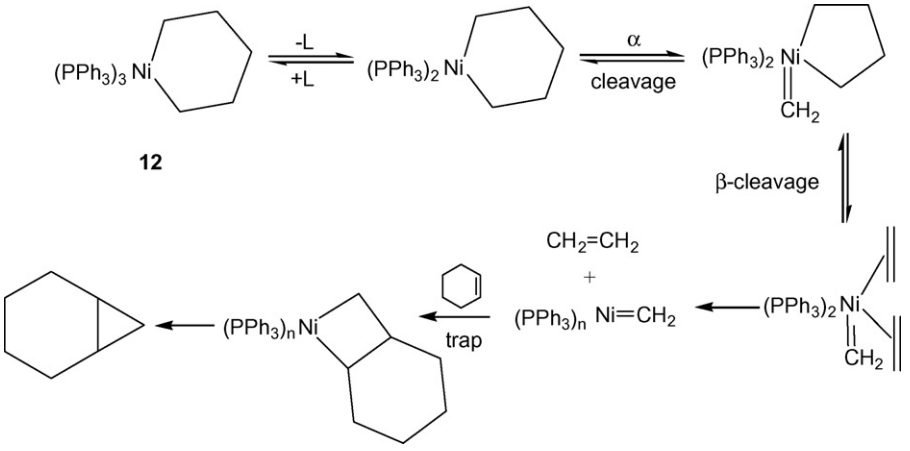


(13)

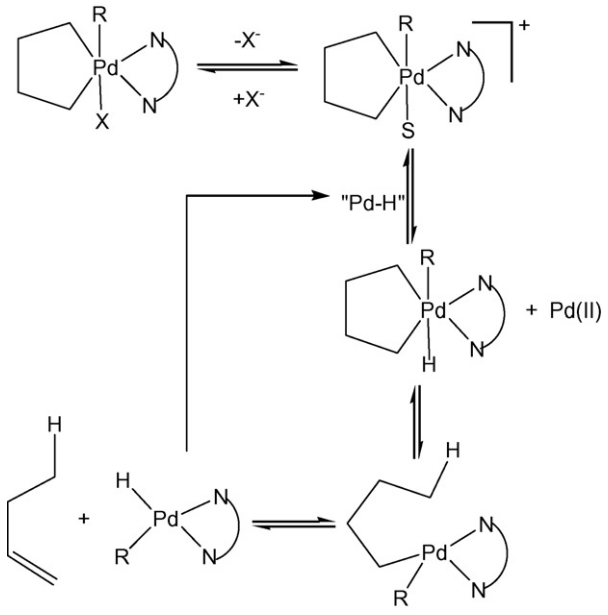
2.5. Other pathways

2.5.1. Intermolecular chain reactions

An intermolecular chain reaction was first proposed in a study on the mechanism of the thermal decomposition of

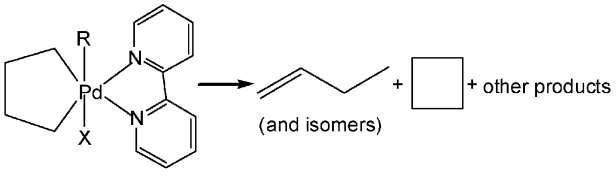


Scheme 6.



Scheme 7.

This process was also observed in the decomposition of the pallada(IV)cyclopentane complex **14** forming 1-butene (Eq. (14)), which was then proved by a deuteration study [42]. The proposed mechanism for the formation of butenes is shown in Scheme 7.

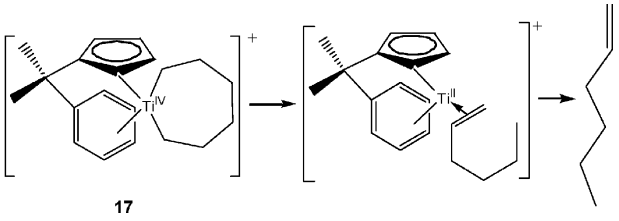


(14)

2.5.2. Concerted transition-metal-assisted β-hydride transfer

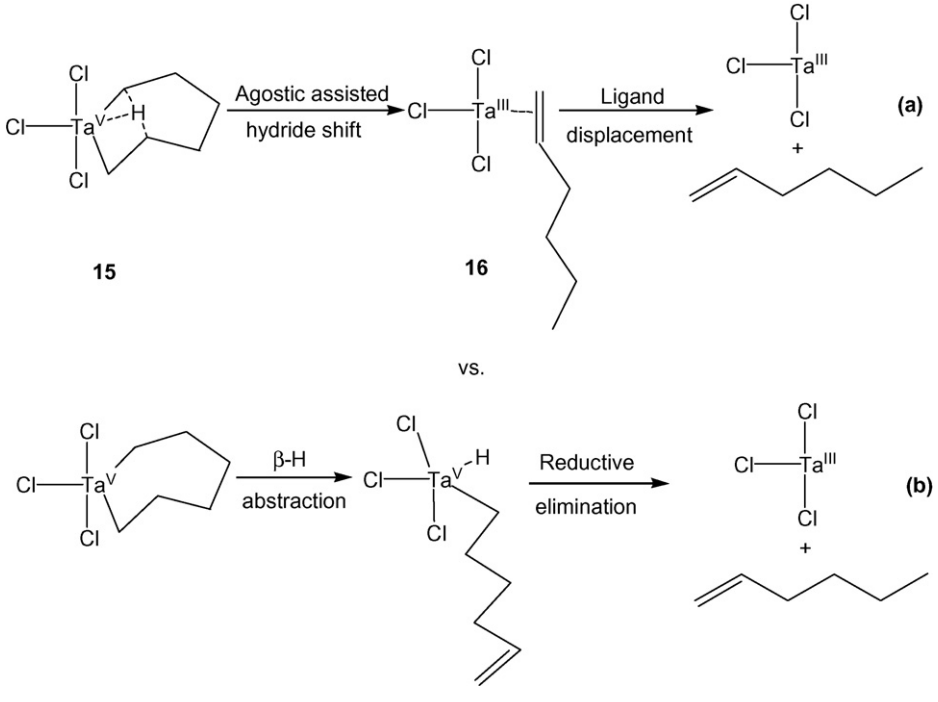
Yu and Houk [26] recently considered such a mechanism, on which MP2 and B3LYP calculations were carried out, as an alternative to the conventional two-step metallacycle decomposition mechanism postulated by Whitesides and co-workers [17,18]. The theoretical results suggested that the conversion of tantalacycloheptane **15** to a tantalum-(1-hexene) complex **16** could go via a novel concerted process (**a**) described in Scheme 8 [21]. The authors found that the concerted route was favoured over the conventional two-step route (**b**), in which the reductive elimination step is particularly unfavourable [26].

Decomposition of the conformationally flexible seven-membered titana(IV)cycloheptane **17**, to yield 1-hexene, takes place via the concerted transition metal-assisted β-hydrogen transfer [24,27]:

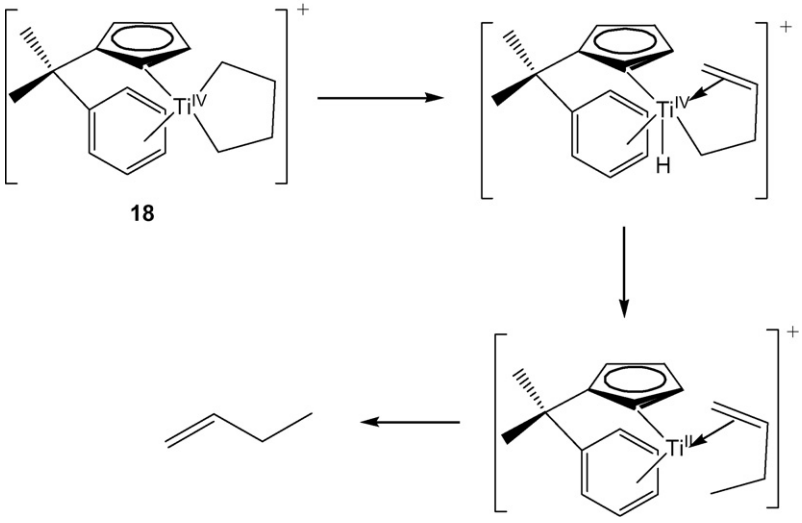


(15)

The decomposition of **18**, the rigid five-membered titana(IV)cyclopentane to 1-butene was proposed to occur from computational studies in a stepwise route which involves β-hydrogen abstraction and subsequent reductive C–H elimination (Scheme 9).



Scheme 8.



Scheme 9.

3. Decomposition conditions and products

Most of the decomposition studies on metallacycloalkanes reported so far were carried out in a solvent in which decomposition reactions can easily take place and temperatures were generally low. On the other hand, decomposition in solid and gas phases will be interesting since no solvent molecules are present to interfere with the decomposition pathways. However, these experiments are largely unexplored, due to instrumental and other limitations [7]. The experimental conditions such as temperature, solvent, and mode of heating will play a significant role in the formation of a variety of products and in different compositions.

3.1. Decomposition in solvent

Thermal decomposition studies in a solvent are usually carried out in the following way: the metallacycloalkane complexes are dissolved in the appropriate solvent and the resulting solutions are heated in sealed tubes in a thermostable oil bath for a specific time. The resulting decomposition products can then be analysed by gas chromatograph equipped with a flame ionization detector (GC-FID) or with a mass spectrometer detector (GC–MS). These decomposition reactions are carried out under anhydrous, oxygen-free conditions. Experimental conditions and decomposition products of metallacycloalkanes are given in Table 1

.

3.1.1. General decomposition conditions

Table 1 summarises the products obtained from the thermal decomposition of metallacycloalkanes under the given experimental conditions.

In Table 1, platinacyclopentanes (**A**) and platinacyclohexanes (**B**) were decomposed in methylene chloride at 120 °C, while platinacycloheptanes (**C**) were decomposed at 60 °C to give, in each case the corresponding alkenes [17,18]. Thermal decomposition in cyclohexane of bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes (**D**) produced 1,1-dimethylcyclopropane at 126 °C [31]; whereas bis(tricyclopentylphosphine)-platinacyclopentane (**E**) yielded 1-butene as the major product at 99 °C [41]. At 177 °C, bis(trialkylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (**F**) yielded two major products: namely 2,2,3,3,-tetramethylbutane and 1-methyl-1-*tert*-butylcyclopropane [43].

Toluene is the solvent in which most thermal decompositions of nickel and palladium metallacycloalkanes have been carried out. Bis(phosphine)-3,3-dimethylinickela-cyclobutane (**G**) decomposed when heated, undergoing competitive carbon–carbon bond cleavage to give isobutene and ethylene, with reductive elimination affording 1,1-dimethylcyclopropane and skeletal isomerization of the metallacyclic ring yielding 3-methyl-1-butene, whereas the palladium analog (**H**) gave no significant amount of carbon–carbon bond cleavage products [38]. Thermolysis (9 °C) of phosphine nickel metallacyclopentanes (**I–K**) produced ethylene, cyclobutane or butenes depending on the coordination number [36]. Thermal decomposition of palladacyclopentane derivatives of the type of $L_2Pd(CH_2)_4$ (**L**) gave butenes as the major products, whereas cyclobutane (for L = PPh_3) and ethylene (for L_2 = dppe or dcpe) are formed as minor products [44].

Thermal decomposition of the rhenacyclopentane $(CO)_2CpRe(CH_2)_4$ (**M**) [45] in benzene-d_6 solution at 100 °C was rapid and gave methylcyclopropane (67%). In contrast, the cobaltacyclopentane compound $CpCo(PPh_3)(CH_2)_4$ (**N**) decomposed in benzene solution at room temperature giving a mixture of 1-butene (11%), *trans* 2-butene (64%) and *cis* 2-butene (25%) [46].

3.1.2. Induced decomposition conditions

Under certain conditions, thermal decompositions can be induced to give more selective products than those obtained under normal conditions.

Oxidation induced rapid decomposition of the phosphine nickelacyclopentane complexes to cyclobutane (e.g.

Table 1
General experimental conditions[a] and products of decomposition of metallacycloalkanes

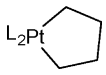
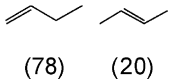
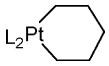
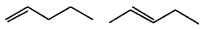
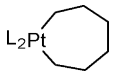
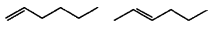
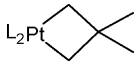
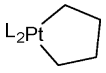
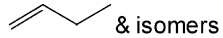
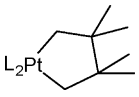
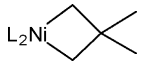
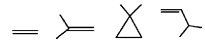
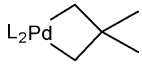
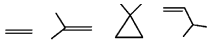
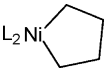
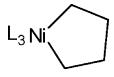
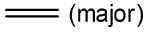
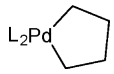
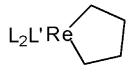
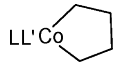
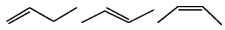
Type of compound	Ligand	Solvent[b]	Temperature (°C)	Products (%)	References
A 	L: PPh_3; L_2: dppe	Methylene chloride	120	 (78) (20)	[17,18]
B 	L: PPh_3; L_2: dppe	Methylene chloride	120	 (75) (17)	[17,18]
C 	L: PPh_3; L_2: dppe	Methylene chloride	60	 (83) (17)	[17,18]
D 	L: PEt_3, P^iPr_3, PCy_3	Cyclohexane	126	 (94 – 98)	[31]
E 	L: PCy_3	Cyclohexane	99	 & isomers (60 – 93)	[41]
F 	L: PEt_3	Cyclohexane	177	 (12) (88)	[43]
G 	L: PPh_3; L_2: dpe	Toluene	24	 (15) (26) (47) (6)	[38]
H 	L: PPh_3	Toluene	60 & 85	 (5) (12) (74) (4)	[38]
I 	L: PPh_3	Toluene	9	 (major)	[36]
J 	L: PPh_3, PCy_3; L_2: dppe	Toluene	9	 (major)	[36]
K 	L: PPh_3	Toluene	9	 (major)	[36]

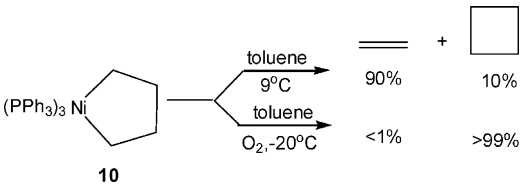
Table 1 (*Continued*)

Type of compound	Ligand	Solvent[b]	Temperature (°C)	Products (%)	References
L 	L: PPh_3; L_2: dppe, tmen, bipy, dcpe	Toluene	60	Butenes (major)	[44]
M 	L: CO; L′: Cp	Benzene-d_6	100	 (67)	[45]
N 	L: Cp; L′: PPh_3	Benzene	Room temperature	 (11) (64) (25)	[46]

[a] General decomposition conditions here are compared to induced decomposition conditions described in Section 3.1.2, which means the metallacycloalkane complexes decomposed in solvent at various temperatures in the absence of air.

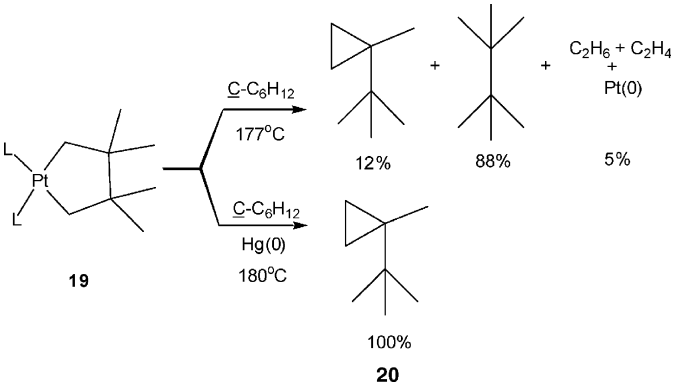
[b] The solvents mentioned in the table were used in most cases, for others see Eqs. (22)–(24).

Eq. (16)) [36].



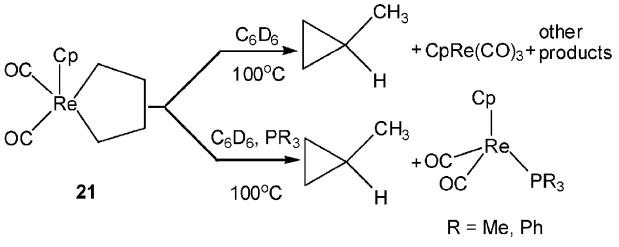
(16)

By poisoning with mercury [43], the thermal decomposition of bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane **19** was induced to generate 1-methy-1-*tert*-butylcyclopropane **20**, the product of a homogeneous reaction sequence:



(17)

In comparison to decomposition in benzene-d_6 as mentioned above, the decomposition products of the rhenacyclopentane $(CO)_2CpRe(CH_2)_4$ **21** were methylcyclopropane and $CpRe(CO)_2PR_3$ in the presence of PR_3 [45]:

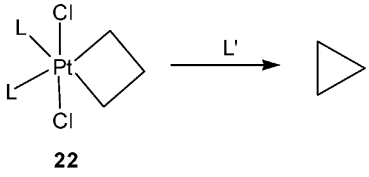


(18)

Table 2
Decomposition of the palladacyclopentanes of type of $L_2Pd(CH_2)_4$ induced by $Bu^n{}_2O{\cdot}BF_3$

Ligand (L)	*n*-C_4 distribution (%)			
	1-Butene	*n*-Butane	2-Butene (*cis*)	2-Butene (*trans*)
dppe	1.6	47.9	11.2	39.0
tmen	1.7	50.0	12.1	36.0
bipy	3.2	20.9	15.4	58.1
PPh_3	4.7	4.2	20.9	70.2

The presence of π-acceptor ligands, or ligands with a strong *trans* effect favours the reductive elimination of metallacycles [11,47]. Thus, the addition of phosphines, arsine, stibines or anionic ligands (I^-, SCN^-, CN^-) to otherwise stable platina(IV)cyclobutane complexes **22** can induce their decomposition by reductive elimination:



L' = PR_3, AsR_3, SbR_3, I-, CN-, SCN-, olefins, H_2O, CO etc.
L = nitrogen donor ligand, THF

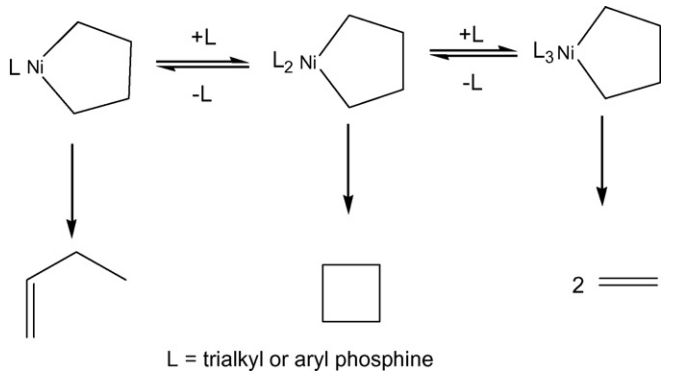
(19)

The decomposition of palladacyclopentanes is induced by $Bu^n{}_2O{\cdot}BF_3$ to give an increased amount of *n*-butane and extensive isomerization to 2-butenes (Table 2) [44].

3.1.3. General factors affecting thermal stability

As the stability of the metallacycles is quite dependent on the nature of metal, size of the ring, solvent and supporting ligands, the following factors also have their significance in thermal studies of various metallacycles.

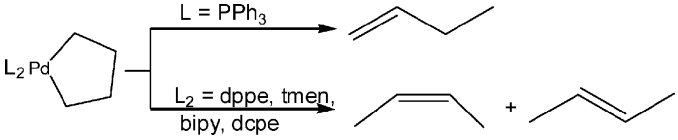
3.1.3.1. Effect of ligand. The nature of the ligands affects the activity and selectivity of ethylene oligomerisation catalysts. For



Scheme 10.

example, PNP ligands having bulky *ortho* alkyl–phenyl groups favour 1-hexene formation, whereas in the absence of *ortho*-substitution of the phenyl rings, 1-octene formation is favoured [22,48]. The effect of ligands also plays an important role in the decomposition pathway in metallacyclic systems. Palladacyclopentanes of the type of $L_2Pd(CH_2)_4$ [44], which have been mentioned above, with different ligands give different products when they decompose in toluene.

Butenes were the major products in all cases when heating at 60 °C, but 1-butene predominated when the ancillary ligand was a phosphine, and 2-butenes were the major products in the other cases:



(20)

Besides the nature of the ligands, coordination number of the metal has an effect on the decomposition. It is well known that the mechanism of decomposition of nickelacyclopentanes in solvent is strongly dependent on the coordination number of the nickel, leading to the formation of *n*-butenes, cyclobutane or ethylene, for 3-, 4- or 5-coordinate nickel, respectively (Scheme 10) [36,37,49].

Our recent studies showed that the thermal stability of metallacycles is dependent on the ligand systems and that this affects the decomposition mechanism. Thus, the PPh_3 containing compounds are quite sensitive to the temperature changes, and the order of stability for Pd and Pt compounds is as follows: $PPh_3 < P^tBu_3 <$ diphos (diphos = dppe, dppp, dmpe, dcpe). The significant increase in stability of diphos containing metallacycles can be explained by the chelating nature of the ligands. The role of the ligands in determining the decomposition pathways is observed as shown in Table 3 [15].

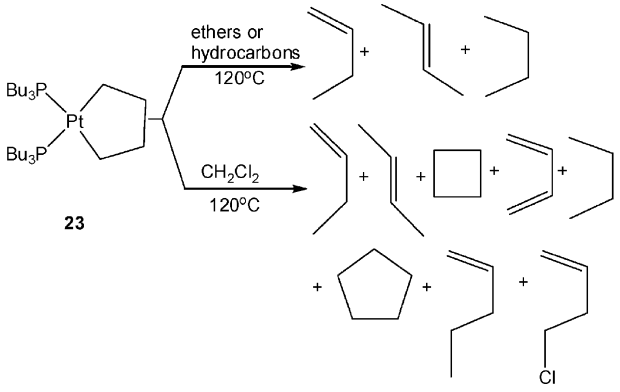
The thermal decomposition of dppp and P^tBu_3 containing platinacyclononanes was carried out in cyclohexane at 170 °C for 2 h. 1-Octene was the major product (52%) in both cases. With the chelating ligand dppp, the formation of *n*-octane was quite significant (24%), whereas, the yields of 2-octenes (*trans* and *cis*) and 1,7-octadiene were slightly higher in the P^tBu_3 complex [15].

Table 3
Decomposition of the platinacyclononanes in cyclohexane at 170 °C for 2 h[a]

Ligand (L)	*n*-C_8 distribution (%)				
	1-Octene	*n*-Octane	2-Octene	3-Octene	Octadiene
dppp	52	24	17	6	<1
P^tBu_3	52	14	26	7	8

[a] These thermal decomposition studies were carried out under anhydrous, oxygen-free conditions. Decomposition in solid phase employed ca. 10 mg samples of each complex and 0.02 M solutions in cyclohexane in a sealed evacuated tube. The tubes were then heated in a oil bath at 170 °C (±5 °C) for 2 h. Decomposition products were analysed by GC-FID and GC–MS.

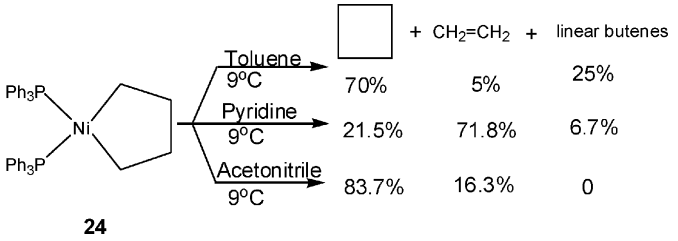
3.1.3.2. Effect of solvent. In the case of platinacyclopentanes [29], thermal decomposition of 1,4-tetramethylenebis(tri-*n*-butylphosphine)platinum(II) **23** at 120 °C in non-halogenated solvents (diethyl ether, tetrahydrofuran, *n*-hexane, cyclohexane) yielded only butenes and butane. However, decomposition of this compound in methylene chloride solution proceeded more rapidly and yielded significant quantities of cyclobutane, cyclopentane, 1-pentene and 5-chloro-1-pentene:



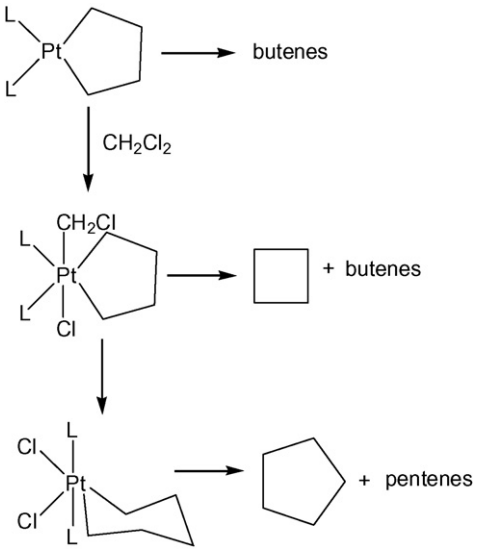
(21)

The decomposition pathway leading to cyclobutane can be explained by the oxidative addition of a solvent molecule (methylene chloride) to platinum(II) to give a platinum(IV) intermediate, which can then form cyclobutane by reductive elimination, while it undergoes the normal decomposition pathway in non-halogenated solvents (Scheme 11) [29].

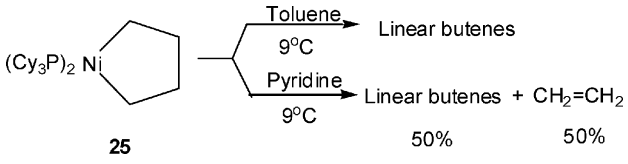
The decomposition pathway for nickelacyclopentanes with different phosphine ligands, as a function of solvent, is shown in the following equations [36]:



(22)



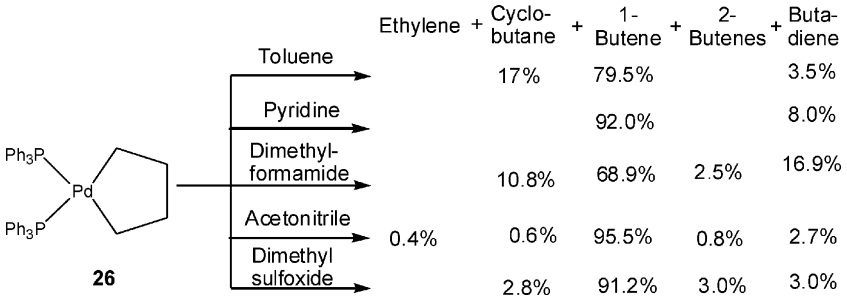
Scheme 11.



(23)

Ethylene became the major product when the bis(triphenylphosphine) complex **24** was decomposed in pyridine. The tricyclohexyl phosphine complex **25**, which produced only linear butenes on decomposition in toluene, gave a 50% yield of ethylene in pyridine.

The effect of solvent upon the decomposition products of the palladium analog **26**, of complex **24** has also been investigated [44]. Decomposition reactions in each solvent were carried out by heating the compound at 60 °C for 5 h, with an initial concentration of 8×10^{-3} mol dm^{-3}. 1-Butene and 2-butene were the major constituents of the product mixture in all cases, but the cyclobutane content was significant when poorly co-ordinating solvents such as toluene and dimethylformamide were used, and dropped to low levels when highly co-ordinating solvents such as pyridine, acetonitrile and dimethyl sulfoxide were used:



(24)

The halogenated solvents yielded mainly hydrocarbons and the halogenated metal salts during the thermolysis reactions but not halogenated organic products, when the metallacycloalkane compounds were heated up to 175 °C for 2 h in dichloromethane [15].

Table 4
Decomposition of rhodacycloalkanes[a] and platinacycloalkanes[b] in solid state at 170 °C for 2 h[c]

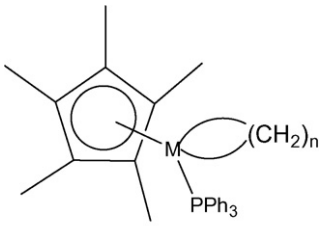
Metal (M)	Ring size (n)	Observed products (%)				
		1-Alkene	n-Alkane	2-Alkene	3-Alkene	Diene
Rh	8[d]	20	19			
Rh	10[e]	60	26			
Pt	8	45	32	14		8
Pt	9	44	21	19	12	4

[a] L = Cp* and PPh_3.
[b] L = dppp.
[c] Experimental conditions see Table 3.
[d] Cyclohexane = 61%.
[e] Cyclooctane = 14%.

3.1.3.3. Effect of changes of metal and its oxidation state. The thermal stability of M–C bonds of organometallic compounds generally increases on descending a triad, e.g. for Groups 8, 9 and 10, which is in contrast to the situation for the main group metals where M–C bond strengths significantly decrease [50]. It is clearly observed that thermal stability of 3d transition metal containing metallacycles are relatively unstable in comparison with their 4d and 5d analogues. For example, t_{dec} = 9 °C for bis(triphenylphosphine)nikelacyclopentane **24** [36], 60 °C for its palladium analog **26** [44] and 120 °C for the platinum analog **1a** [17,18]. Different decomposition products were also formed with different oxidation states, e.g. compare Pd(II) and Pd(IV) compounds, 2-butenes were obtained as major thermal decomposition products for Pd(II)cyclopentane [44] with bipy ligand, while reductive elimination to form cyclobutane was favoured for the Pd(IV) analogue **14** [42].

3.1.3.4. Effect of the size of the ring. Medium ring compounds with 7–11 members and larger ring compounds are more difficult to make [8] and this can in part be due to their decreased thermal stability. For example, Whitesides et al. found that five- and six-membered ring metallacycles are much more stable than the seven-membered metallacycles [17,18]. Despite this, we have prepared a variety of medium to large metallacycloalkanes with various ligand systems by an alternative route [51] to study the effect of the ring size on the organic product distribution on thermolysis [15].

From the results presented in Table 4, it is clear that the distribution of organic products produced upon decomposition of rhodacycloalkanes in the solid state at 170 °C was significantly dependent on the ring size. The formation of 1-alkenes



M = Rh, n = 4, 5, 6;
M = Ir, n = 4, 5

Fig. 2. Rhodium(III) and iridium(III) metallacycloalkane complexes. M = Rh, n = 4–6; M = Ir, n = 4, 5.

is much more favourable for the 10-membered ring compound, while the α-C–C cleavage followed by reductive elimination route to form cycloalkane was much easier in the 8-membered ring. In the case of platinacycloalkanes, however, the decomposition product distributions for the two different ring sizes were not found to be significantly different except that 3-alkene was not observed in the decomposition of the eight-membered ring compound.

3.2. Decomposition in the solid and gas phase

Although few decomposition studies have been carried out in the solid and gas phases, there is an obvious advantage that metallacycloalkanes may be studied in the absence of solvent interactions of various kinds.

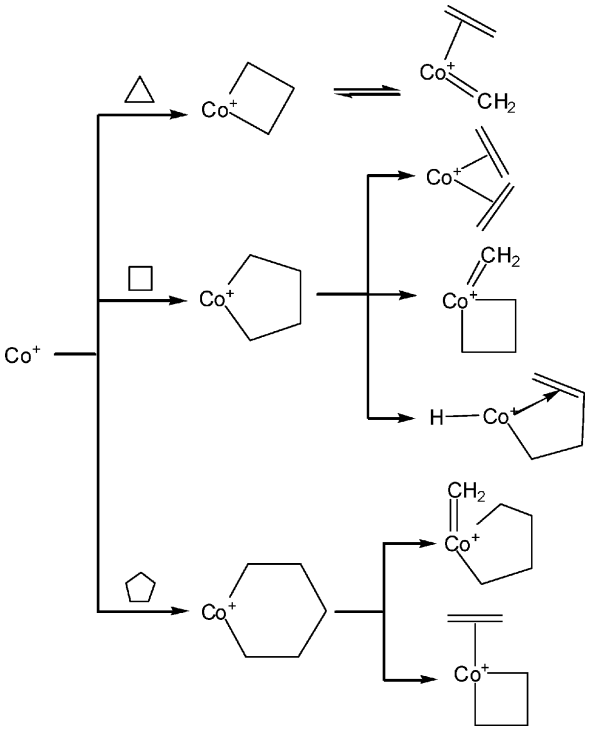
Decomposition of metallacycloalkane compounds as a solid can be carried out in two ways. One is direct heating the solid sample under vacuum and the other is using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Mashima and Takaya studied the decomposition of compounds **27a** and **27b** [52]. Solid **27a** decomposed when heated rapidly to 200 °C under vacuum to give ethylene, 1,3-butadiene, and methylcyclopropane by β-carbon–carbon bond cleavage. The 1,3-diene $CH_3CH_2C(=CH_2)CH_2{=}CH_2$ which is derived from the decomposition of a six-membered metallacycle was also formed [53]. In contrast, the main decomposition product of **27b** was the diene, $CH_3CH_2C(=CH_2)CH_2{=}CHPh$ (Scheme 12).

The thermal decomposition of rhodium(III) and iridium(III) metallacycloalkane complexes (Fig. 2) was studied by DSC and TGA [54].

In all cases three decomposition steps were identified, the first being the release of the C_nH_{2n} moiety giving the corresponding n-alkenes as the major product, which was confirmed by GLC analysis of the gases leaving the thermobalance during this step; the second, the release of a C_5Me_5 group followed by the third with the release of PPh_3.

Decomposition of naked gas-phase metallacyclic ions is believed to provide some fundamental information [7]. Armentrout and Beauchamp [55] using both an ion cyclotron resonance (ICR) spectrometer and an ion beam instrument, studied the formation and decomposition of cobalt metallacycles. This study showed the ring cleavage reactions in all cases (Eq. (25)) and suggested that symmetric or nearly symmetric C–C bond cleavage was preferred:

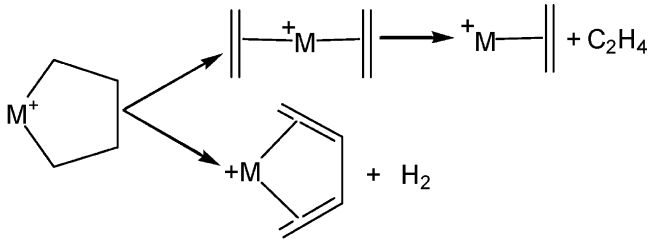


(25)

Jacobson and Freiser [7] reported a study on the generation and decomposition processes for gas-phase group 8 metal (Fe, Co, Ni) metallacyclic ions using Fourier transform mass spectrometry (FTMS).

In this study, Fe^+ decarbonylated cyclobutanone to generate a stable metallacyclobutane ion, which decomposed by the low energy pathway (either β-hydride transfer or reductive elimination of cyclopropane) competing with the high-energy pathway (initial rearrangement to a carbene ethene complex, followed by elimination of ethene). However, both Ni^+ and Co^+ generated unstable metallacyclobutane intermediates.

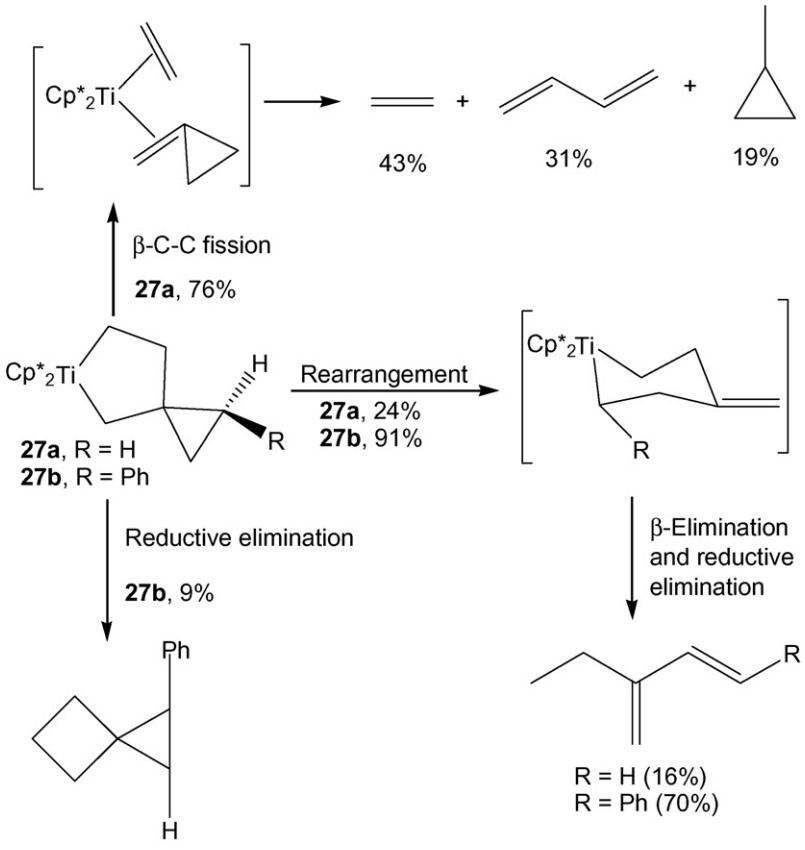
Metallacyclopentane ions decomposed by both symmetric ring cleavage and dehydrogenation processes:



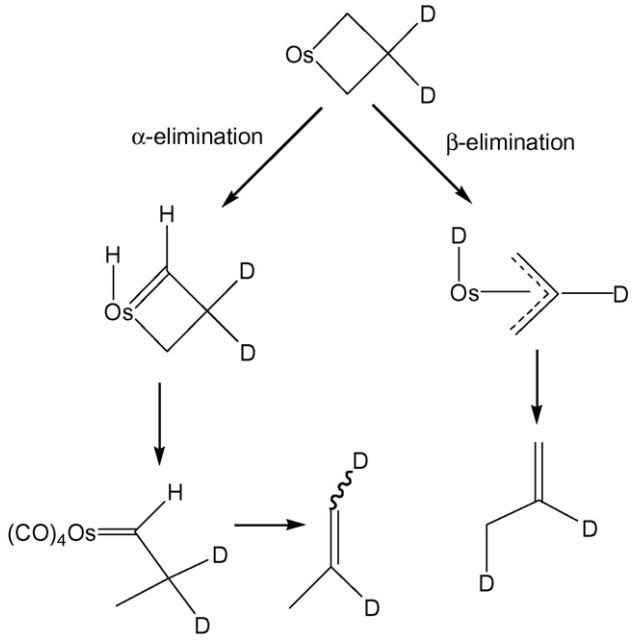
M= Fe, Co, Ni

(26)

In contrast, the metallacyclohexane ions appeared to decompose by an initial 1,4-hydrogen atom shift generating an activated (1-pentene) metal ion complex:

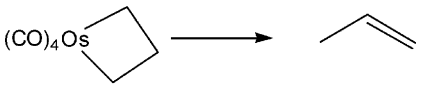


Scheme 12.

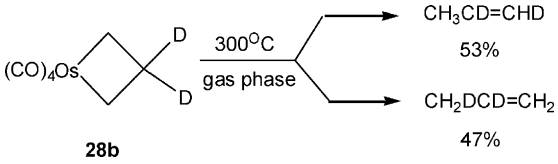


Scheme 13.

Thermal decomposition of the osmacyclobutane compound **28a** gives propylene under all conditions [35]. However, the authors found that intermolecular products and secondary reactions occurred when the osmacyclobutane compound **28b** was decomposed in C_6D_6 solution. In order to preclude secondary reactions, the thermal decomposition of **28a** was carried out in gas phase (Eqs. (28) and (29)), and results indicated that both α- and β-hydride elimination mechanisms are operative (Scheme 13).

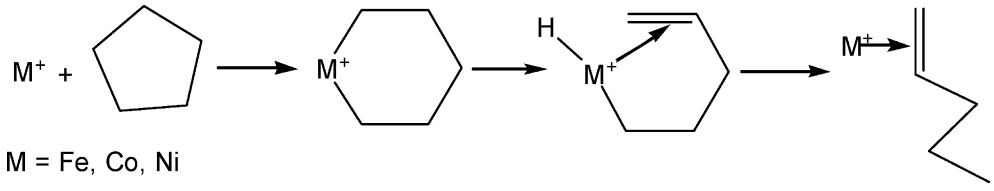


28a (28)



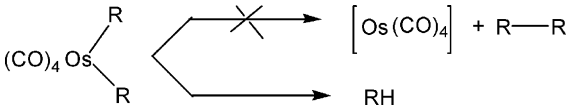
28b (29)

No reductive elimination products were reported to be found in this study. Interestingly, this finding is consistent with a study



(27)

on the decomposition of dialkyl osmium, $Os(CO)_4R_2$, in which the most significant result is the absence of simple intramolecular reductive elimination and products are RH [56]:



(30)

4. Conclusions

A large number of small metallacycloalkanes with a variety of metals have been reported, particularly since the 1970s. Recently, there has been considerable interest in the preparation of medium to large metallacycloalkanes, partly because they are key intermediates in various catalytic transformations. The thermal decomposition patterns of these compounds can give new information on the formation of a variety of organic products. Because of their high reactivity, these compounds can yield unexpected products in the presence of reactive substrates, which may be difficult to produce by conventional routes, e.g. formation of *n*-alkanes, cycloalkanes, 1-alkene, 2-alkene and dienes from dihaloalkanes through metal mediation. To yield the organic products, metallacycles can go through conventional decomposition pathways such as β-hydride elimination, etc. or certain pathways only proposed in metallacyclic systems. Thermal decomposition products strongly depend on the nature of the metal, ligand systems, ring size, as well as the decomposition conditions. Currently our research is concentrated on the insertion of small molecules into the metal–carbon bonds of metallacycloalkanes as well as explaining the thermolysis reactions.

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References

[1] (a) I. Omae, Organometallic Intramolecular-coordination Compounds, Elsevier Science Publ., Amsterdam, Netherlands, 1986;
(b) I. Omae, Coord. Chem. Rev. 248 (2004) 995.
[2] (a) P.J. Davidson, M.F. Lappert, R. Pearce, Chem. Rev. 76 (1976) 219;
(b) G.G. Choudhry, O. Hutzinger, Toxicol. Environ. Chem. 5 (1982) 97.
[3] (a) A. Govindaraj, C.N.R. Rao, Pure Appl. Chem. 74 (2002) 1571;
(b) C.N.R. Rao, A. Govindaraj, Acc. Chem. Res. 35 (2002) 998.
[4] S. Hirano, T. Yogo, Koatsuryoku no Kagaku to Gijutsu 1 (1992) 99.
[5] (a) P.A. Dowben, J.T. Spencer, G.T. Stauf, Mater. Sci. Eng. B: Solid-State Mater. Adv. Technol. B 2 (1989) 297;
(b) O.L. Alves, C.M. Ronconi, Quimica Nova 25 (2002) 69.
[6] L.F. Zharovskii, L.V. Zavyalova, G.S. Svechnikov, Thin Solid Films 128 (1985) 241.
[7] D.B. Jacobson, B.S. Freiser, Organometallics 3 (1984) 513.
[8] B. Blom, H. Clayton, M. Kilkenny, J.R. Moss, Adv. Organomet. Chem. 56 (2006) 149.
[9] R.H. Grubbs, A. Miyashita, J. Am. Chem. Soc. 100 (1978) 7418.
[10] A.K. Tomov, J.J. Chirinos, D.J. Jones, R.J. Long, V.C. Gibson, J. Am. Chem. Soc. 127 (2005) 10166.
[11] B.L. Stocker, J.O. Hoberg, Organometallics 25 (2006) 4537.
[12] J. Cámpora, P. Palma, E. Carmona, Coord. Chem. Rev. 193–195 (1999) 207.
[13] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987, p. 459.
[14] (a) R.H. Grubbs, A. Miyashita, Fundam. Res. Homogeneous Catal. 3 (1979) 151;
(b) R.J. Puddephatt, Coord. Chem. Rev. 33 (1980) 149;
(c) R.J. Puddephatt, Comments Inorg. Chem. 2 (1982) 69;
(d) E. Lindner, Adv. Heterocycl. Chem. 39 (1986) 237.
[15] A. Sivaramakrishna, F. Zheng, J.R. Moss, Unpublished results, 2007.
[16] F. Zheng, J.R. Moss, A. Sivaramakrishna, Poster Abstracts of the 37th International Conference on Coordination Chemistry (ICCC), 2006, p. 450.
[17] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 95 (1973) 4451.
[18] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.
[19] P. Diversi, G. Ingrosso, A. Lucherini, J. Chem. Soc. Chem. Comm. (1978) 735.
[20] R. Emrich, O. Heinemann, P.W. Jolly, C. Krueger, G.P.J. Verhovnik, Organometallics 16 (1997) 1511.
[21] J.T. Dixon, M.J. Green, F.M. Hess, D.H. Morgan, J. Organometal. Chem. 689 (2004) 3641 (and references therein).
[22] A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Neveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, J. Am. Chem. Soc. 126 (2004) 14712.
[23] M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, J. Am. Chem. Soc. 127 (2005) 10723.
[24] T.J.M. de Bruin, L. Magna, P. Raybaud, H. Toulhoat, Organometallics 22 (2003) 3404.
[25] S. Tobisch, T. Ziegler, Organometallics 22 (2003) 5392.
[26] Z. Yu, K.N. Houk, Angew. Chem. Int. Ed. Engl. 42 (2003) 808.
[27] S. Tobisch, T. Ziegler, Organometallics 24 (2005) 256.
[28] X. Huang, J. Zhu, Z. Lin, Organometallics 23 (2004) 4154.
[29] G.B. Young, G.M. Whitesides, J. Am. Chem. Soc. 100 (1978) 5808.
[30] F. Ozawa, A. Yamamoto, Organometallics 1 (1982) 1481.
[31] R. DiCosimo, G.M. Whitesides, J. Am. Chem. Soc. 104 (1982) 3601.
[32] P. Binger, H.M. Bűch, R. Benn, R. Mynott, Angew. Chem. Int. Ed. Engl. 21 (1982) 62.
[33] P. Binger, M.J. Doyle, R. Benn, Chem. Ber. 116 (1983) 1.
[34] J.T. Burton, R.J. Puddephatt, Organometallics 5 (1986) 1312.
[35] W. Fischer, R.T. Hembre, D.R. Sidler, J.R. Norton, Inorg. Chim. Acta 198–200 (1992) 57.
[36] R.H. Grubbs, A. Miyashita, M. Liu, P. Burk, J. Am. Chem. Soc. 100 (1978) 2418.
[37] R.H. Grubbs, A. Miyashita, J. Am. Chem. Soc. 100 (1978) 1300.
[38] A. Miyashita, M. Ohyoshi, H. Shitara, H. Nohira, J. Organomet. Chem. 338 (1988) 103.
[39] S.L. Buchwald, E.V. Anslyn, R.H. Grubbs, J. Am. Chem. Soc. 107 (1985) 1766.
[40] J.D. Meinhart, E.V. Anslyn, R.H. Grubbs, Organometallics 8 (1989) 583.
[41] T.M. Miller, G.M. Whitesides, Organometallics 5 (1986) 1473.
[42] A.J. Canty, J.L. Hoare, N.W. Davies, P.R. Traill, Organometallics 17 (1998) 2046.
[43] G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.
[44] P. Diversi, G. Ingrosso, A. Lucherini, T. Lumini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1988) 133.
[45] (a) G.K. Yang, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 6500;
(b) G.K. Yang, R.G. Bergman, Organometallics 4 (1985) 129.
[46] Y. Wakatsuki, O. Nomura, H. Tone, H. Yamazaki, J. Chem. Soc. Perkin II (1980) 1344.

[47] P.W. Jennings, L.L. Johnson, Chem. Rev. 94 (1994) 2241.
[48] M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, Chem. Commun. (2005) 622.
[49] R.H. Grubbs, A. Miyashita, M.M. Liu, P.L. Burk, J. Am. Chem. Soc. 99 (1977) 3863.
[50] (a) J.C. Bailar, H.J. Emeléus, S.R. Nyholm, A.F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, vol. 4, Pergamon Press, Oxford, 1973, p. 799;
(b) C. Mancuso, J. Halpern, J. Organometal. Chem. 428 (1992) C8.
[51] (a) K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer, A. Sivaramakrishna, Chem. Commun. (2005) 3865;
(b) A. Sivaramakrishna, H. Su, J.R. Moss, Angew. Chem. Int. Ed. 46 (2007) 3541.
[52] K. Mashima, H. Takaya, Organometallics 4 (1985) 1464.
[53] K. Mashima, N. Sakai, H. Takaya, Bull. Chem. Soc. Jpn. 64 (1991) 2475.
[54] A. Cuccuru, P. Diversi, G. Ingrosso, A. Lucherini, J. Organometal. Chem. 204 (1981) 123.
[55] P.B. Armentrout, J.L. Beauchamp, J. Am. Chem. Soc. 103 (1981) 6628.
[56] W.J. Carter, S.J. Okrasinski, J.R. Norton, Organometallics 4 (1985) 1376.