Metallacyclobutane Complexes of the Group Eight Transition Metals: Synthesis, Characterizations, and Chemistry

Paul W. Jennings* and Lynette L. Johnson

The Department of Chemistry and Biochemistry, Gaines Hall, Montana State University, Bozeman, Montana 59717-0340

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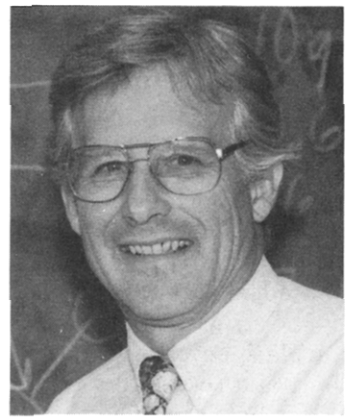
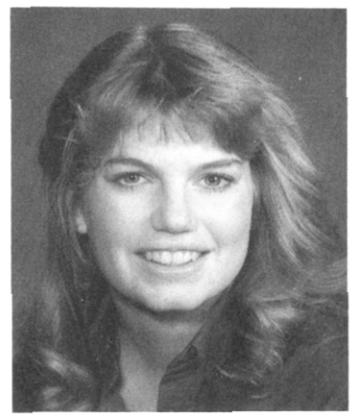


Wyn Jennings was born in Denver, CO, and received has B.S. in Chemistry at the University of Colorado where he did undergraduate research with Dr. John Meek and Dr. Stanley Cristol. This work was further extended to a M.S. degree. In 1964, he received his Ph.D. under the direction of Dr. William Epstein of the University of Utah. Thesis work included the photochemistry of conjugated ketones and the structure elucidation of metabolites from fungi. Subsequently, he spent two years at the California Institute of Technology as a Research Fellow with Dr. Jack Richards working on organometallic photochemistry. In 1966, he joined the faculty at Montana State University and now holds the rank of Professor. Research interests include the organometallic reaction mechanisms and organic transformations using organometallics.



Lynette Johnson was born in Kalispell, MT, and received her B.S. degree in Chemistry at Montana State University. After teaching in high school for two years, she returned to Montana to graduate school where she received a M.S. degree. Her research effort is essentially contained in this review.

I. Introduction

The chemistry of metallacyclobutane compounds has been a major area of organometallic chemistry. Within the past two decades these intriguing systems have been explored in depth and their study has attracted considerable attention. Metallacyclobutane compounds also play an important role in a number of catalytic transformations. Further, they have been suggested as key intermediates in olefin and acetylene metathesis,[1–11] cycloadditions of alkenes[12–15] and

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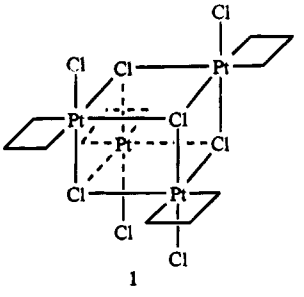
cyclotrimerizations of acetylenes,[16-18] dimerization of alkenes,[19-21] oligomerization of alkynes,[22,23] oligomerization of dienes,[24-27] polymerization of olefins and acetylenes,[28-31] and isomerizations of strained carbocyclic ring systems.[32-35] Finally, in addition to being key intermediates in catalytic reactions, metallacyclobutanes also have been used successfully in organic synthesis.[36]

The first metallacyclobutane compound was discovered in 1955 by Tipper.[37] While studying the similarities in electron delocalization between cyclopropanes and olefins suggested by Walsh in 1949,[38] Tipper examined the ability of cyclopropane to form complexes with transition metals analogous to known olefin–metal π complexes. He treated cyclopropane with hexachloroplatinic acid (H_2PtCl_6), in acetic anhydride, and found the reaction product to have the empirical formula $PtCl_2C_3H_6$ (**1**). Further, reaction of **1** with pyridine formed a stable compound of formula $(C_5H_5N)_2PtCl_2C_3H_6$. Tipper believed the cyclopropane ring remained intact and that the new complex was an edge-bound dimer analogous with Zeise's dimer. The structure of **1** was not accurately identified as a platinacyclobutane, however, until 1960 when Chatt and co-workers further examined the compound.[39] Chatt observed that the solubility properties and the IR data of Tipper's complex suggested a polymeric species, rather than a dimer and that the cyclopropane ring had opened forming a platina(IV)cyclobutane complex. This conclusion was subsequently confirmed by Gillard et al. in 1966,[40] and the structure of compound **1** was suggested to be tetrameric in 1969.[41] Many metallacyclobutane compounds since have been discovered as stable complexes from a variety of methodologies.



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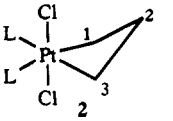
Other comprehensive and semicomprehensive reviews that include discussions on metallacyclobutane compounds have appeared emphasizing topics such as the preparations and properties of metallacyclic compounds,[42-44] metallabenzenes,[45] pallada(II)- and platina(II)cyclobutanes,[46] platina(II)- and -(IV)cyclobutanes,[47] cyclometalation reactions,[48,49] the chemistry of alkanes[50] acetylenes[51] and cyclopropanes,[52] and metallacycles as intermediates in olefin metathesis[1-8] and other metal-catalyzed reactions.[34,53-59] This review will deal specifically with the preparation, characterization, and chemistry of metallacyclobutane derivatives of the group eight transition metals (groups eight, nine, and ten). The discussion is limited to monometallic systems and to ring systems consisting only of metal and carbon atoms.

II. Synthesis of Metallacyclobutane Derivatives

A. Carbon–Carbon Bond Cleavage

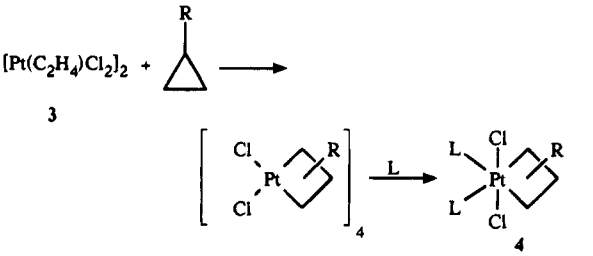
Platinum(II) as the Reagent. Oxidative addition of a C–C bond of cyclopropane to a metal center provides a facile synthesis of metallacyclic complexes of a variety of transition metals. As stated in the introduction, Tipper initiated this methodology when he allowed chloroplatinic acid and cyclopropane to react in acetic anhydride.[37] The resulting tetramer further reacts with several nitrogen donor ligands (L = Py, 2-, 3- and 4-Mepy, 2,6-diMepy, bipy, and en) to yield the platina(IV)cyclobutane derivative **2**.



2

Most often, the chlorine atoms are trans to one another. Although this particular platinum species (H_2PtCl_6/HOAc) provides a facile route to an unsubstituted platina(IV)cyclobutane, it has been ineffective in the synthesis of alkyl or aryl-substituted platina(IV)cyclobutanes.[60]

There exists a more general reagent involving the reaction of various cyclopropanes. Zeise's dimer (**3**) as the platinum(II) source readily forms the tetrameric platina(IV)cyclobutane.[61-63] Subsequent addition of strong electron-donating ligands forms the platina(IV)cyclobutane monomer **4** in high yields (eq 1). Nitrogen donor ligands have been found most

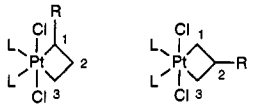


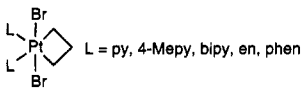
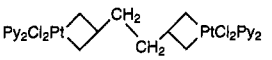
(1)

effective in obtaining the monomeric species **4**. Oxygen donor ligands, such as THF or 1,4-dioxane, may form **4** in solution but are rarely isolated, generally due to their lack of bond strength.[39,41,64] Addition of ligands such as PR_3, DMSO, and CO to the tetrameric complex generally results in reductive elimination of the cyclopropane.[39,61,62,65]

The proposed pathway for platina(IV)cyclobutane formation, shown in Scheme 1, invokes initial coordination of a nucleophilic cyclopropane to an electrophilic Pt(II) center to form the "edge complex", intermediate **5**. Subsequent ring opening of the cyclopropane occurs to form **6**, which upon loss of ethylene and dimerization forms the observed platina(IV)-cyclobutane tetramer **1**. An alternative mechanism, resulting from the suggestion that platinum(IV) is unable to coordinate to olefins, proposes that ethylene is lost from intermediate **5** to form an intermediate analogous to **6** with ethylene removed and solvent occupying the open coordination sites.[64] However, a platina(IV)cyclobutane recently has been synthesized that also accommodates a Pt(IV)–olefin

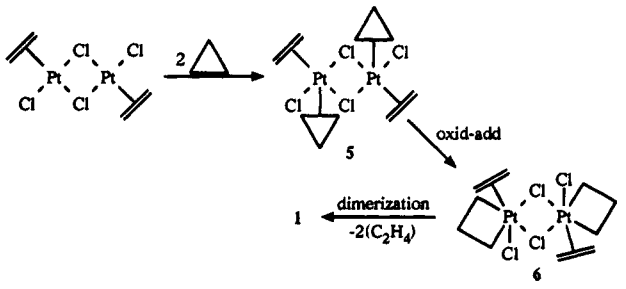
Table 1. Monosubstituted Platina(IV)cyclobutanes via Oxidative Addition



entry	L	R	ref(s)	entry	L	R	ref(s)
1	py	H	63	22	py	2-(4-$EtOC_6H_4$)[a]	75
2	py	2-Me[a]	47,71,74	23	py	2-NH_2	81
3	py	2-Et	69	24	4-Mepy	2-Me[a]	47,74
4	py	2-*i*-Pr	69	25	4-Mepy	1-Ph	75
5	py	2-Bu	47,71,74	26	4-Mepy	2-Ph	75
6	py	2-CH_2CO_2Me	76	27	2-Mepy	2-Ph	75
7	py	2-CH_2OH	77	28	3-Mepy	2-Me[a]	47,74
8	py	2-CHMeOH	77	29	$^1/_2$(bipy)	1-Ph	75
9	py	2-CMe_2OH	77	30	$^1/_2$(bipy)	2-Ph	75
10	py	2-CH_2OMs	78,79	31	$^1/_2$(bipy)	2-CH_2OMs	78,79
11	py	2-CH_2OPNB	79	32	$^1/_2$(tmed)	1-Ph	68,75
12	py	2-CMe_2OPNB	79	33	$^1/_2$(tmed)	2-Ph	75
13	py	1-Ph	68,75	34	$^1/_2$(tmed)	1-Me	80
14	py	2-Ph	61–63	35	$^1/_2$(tmed)	2-Me	80
15	py	2-$PhCH_2$	61–63	36	$^1/_2$(tmed)	2-Et	80
16	py	1-*p*-MeC_6H_4	62,63,75	37	$^1/_2$(phen)	2-Me	47,74
17	py	2-*p*-MeC_6H_4	75	38	THF	2-Me[a]	71
18	py	2-*o*-MeC_6H_4[a]	75	39	THF	1-Ph	64,75
19	py	2-*n*-C_6H_{13}	61–63	40	THF	2-Ph	75
20	py	2-*o*-NO_2Ph	62,63	41	THF	1-*p*-MeC_6H_4	75
21	py	2-(4-$MeOC_6H_4$)[a]	75	42	THF	2-*p*-MeC_6H_4	75
				Complex			
 L = py, 4-Mepy, bipy, en, phen			82,83				84

[a] Found as a mixture with the substituents at the 1 and 2 position. The isomer shown in the table is predominant by a ratio greater than 8 to 1.

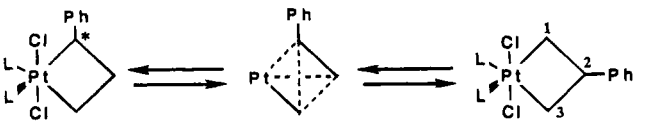
Scheme 1



bond (see eq 9).[66] Further, a recent report on a Zeise's dimer catalyzed reaction invokes a platina(IV)cyclobutane intermediate and suggests that ethylene remains intact upon ring opening[67] (see Scheme 47). Both of these observations lend credence to the mechanism proposed in Scheme 1. It is important to note that several reports refer to platinum–cyclopropane edge complexes. There has been no evidence to date supporting these species. However, the likelihood of such species as transition states or unstable intermediates is quite reasonable. Finally, the question arises as to whether oxidative addition of cyclopropane to platinum is a process that occurs at an edge or at a corner. The evidence to date clearly indicates edge attack. One example, and perhaps the strongest, is shown in eq 2 as the stereochemistry at the cyclopropyl carbon bearing the methyl substituent is maintained. Corner attack would have caused inversion of this carbon moiety. Evidence for the site of attack using other metals is not apparent.

(2)

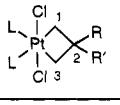
Tables 1–3 include examples of platina(IV)cyclobutanes prepared by this method which is both more convenient than Tipper's synthesis and effective for both alkyl- and aryl-substituted cyclopropanes. Table 1 illustrates a variety of monosubstituted platina(IV)cyclobutanes. In many of the aryl-substituted examples both the 1- and 2-substituted isomers are present. These two species result from the well-known isomerization of platina(IV)cyclobutanes shown as eq 3 for the phenyl-substituted example.[68] A mechanistic discussion for this isomerization is presented in more detail later in the section on intramolecular rearrangements. Briefly, the isomerization is an intramolecular process in which the platinum atom passes over the face of the cyclopropyl moiety in a concerted fashion leading to a new metallacycle as shown. This is often referred to as the Puddephatt rearrangement.



(3)

The most recent studies suggest that Pt(II) inserts into the cyclopropane at the more highly substituted C–C bond, forming a 1-substituted (or α-substituted)

Table 2. 2,2-Disubstituted Platina(IV)cyclobutanes via Oxidative Addition

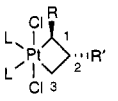


entry	L	R	R′	ref(s)
1	py	Me	Me	69
2	py	Me	CH_2OH	77
3	py	Me	CH_2OMs	78,79
4	py	Ph	CH_2OMs	79
5	$^1/_2$(bipy)	Me	Me	47
6	$^1/_2$(bipy)	Ph	CH_2OMs	79
7	$^1/_2$(phen)	Me	Me	47
8	$^1/_2$(tmed)	Me	Me	80
		Complex		
9				85
	n = 0, 2, 3			

platina(IV)cyclobutane. (There is some ambiguity with regard to nomenclature here. Heterocyclic systems are numbered with the heteroatom being no. 1. However, this field has developed with the no. 1 atom being that atom attached directly to the metal. This is derived from inorganic chelate nomenclature. It is the latter system which shall prevail in this review. Substituents lacking a specific locant should be assumed to be attached to the heteroatom.) Subsequent isomerization then leads to the predominant 2-substituted (or β-substituted) isomer. Although the presence of both isomers and subsequent isomerization in the aryl-substituted examples readily supports this theory, in most of the alkyl-substituted examples only the 2-substituted isomer is observed.[69] It is presumed that Pt(II) inserts into the more highly substituted bond in these latter examples followed by rapid isomerization to the observed species. This presumption is suspect and adequate data to discern this question does not exist. It is extremely important to note that subsequent reaction of the platina(IV)cyclobutane may occur from the less stable isomer. As you will learn later in this review, Pt(II) is participating in this insertion reaction as an electrophile. Thus, it seeks the bond with highest electron density, yielding often the kinetic product. Further, the platina(IV)cyclobutane complex often reacts with cation-like properties. Thus, using microscopic reversibility arguments, one might suggest that a carbocation-like transition state is involved with the oxidative addition process. Subsequent steric factors drive the complex to the thermodynamic product via the intramolecular rearrangement often referred to as the "Puddephatt rearrangement".

When 1,1-disubstituted cyclopropanes are treated with Zeise's dimer, the 2,2-disubstituted platina(IV)-cyclobutanes result (Table 2). (Another example of a 2,2-disubstituted platina(IV)cyclobutane, formed by an alternate methodology, is shown in Scheme 10.[70]) Although in no instance is the 1,1-disubstituted platina(IV)cyclobutane isomer observed in these reactions, it again is not possible to exclude initial insertion of Pt(II) into the more highly substituted bond, followed by rapid isomerization. Again, it is important to emphasize that further reaction may occur from the least stable isomer.

Table 3. Trans-1,2-Disubstituted Platina(IV)cyclobutanes via Oxidative Addition

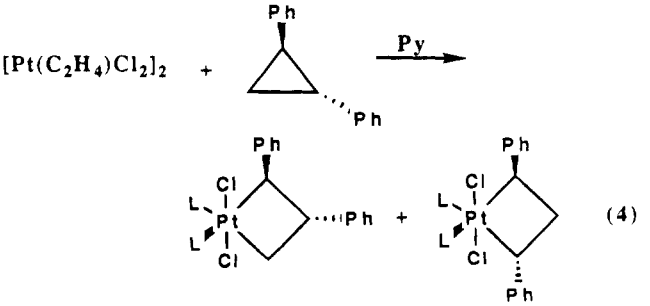


entry	L	R	R′	ref(s)
1	py	Me	Me	69,71,73
2	py	Ph	Ph[a]	61–63,73
3	py	Me	Ph	71,73
4	py	Ph	Me	71,73
5	py	Me	n-Bu	62,63
6	4-(t-Bupy)	Ph	Ph[a]	71,73
7	4-(t-Bupy)	p-MeC_6H_4	p-MeC_6H_4[a]	73,75
8	$^1/_2$(phen)	Me	Me	73
9	CD_3CN[b]	Me	Me	73
10	PhCN[b]	Me	Me	73
11	2-Mepy[b]	Me	Me	73

[a] Found as a mixture with the 1,3-disubstituted isomer, the 1,2-disubstituted isomer being predominant. [b] Isolated at −78 °C.

When Zeise's dimer is added to *trans*-1,2-diarylcyclopropanes, both 1,2-disubstituted and 1,3-disubstituted isomers result (Table 3). The *trans*-1,3-diaryl isomer is observed initially followed by isomerization to the predominant *trans*-1,2-diarylplatina(IV)cyclobutane, strongly supporting Pt(II) insertion into the more highly substituted bond.[71–73] The *trans*-1,2-dialkylcyclopropanes are observed to form only the *trans*-1,2-dialkyl-substituted platinum(IV) product. Investigations to fully elaborate and generalize the stereochemistries and conformations of these products are lacking.

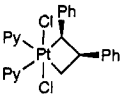
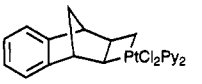
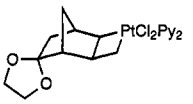
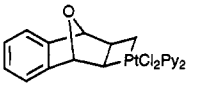
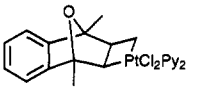
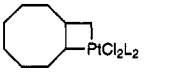
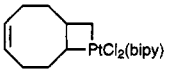
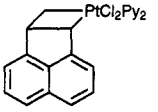
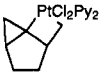
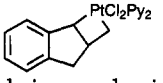
Insertion of Pt(II) into cyclopropane derivatives has been shown to proceed stereospecifically with retention of configuration of the cyclopropane ring substituents.[61,62,86] For example, *trans*-1,2-diphenylcyclopropane oxidatively adds to the Pt(II) center of Zeise's dimer to form a 1,2-diphenylplatina(IV)-cyclobutane, along with the 1,3-diphenyl isomer, each with trans stereochemistry (eq 4). This result is further confirmed by reductive elimination to the original trans-disubstituted cyclopropane.



(4)

Historically, Zeise's dimer was a substantial improvement over platinic acid, but it too appeared to have limitations. All of the examples of 1,2-disubstituted platina(IV)cyclobutanes shown in Table 3 were derived from substrates with trans stereochemistry. However, cis-disubstituted cyclopropanes treated with Zeise's dimer behaved quite differently. For example, upon reaction of *cis*-1-*n*-butyl-2-methylcyclopropane with Zeise's dimer no platina(IV)-cyclobutane derivative was observed.[62] The resulting

Table 4. Cis-Disubstituted Platina(IV)cyclobutanes via Oxidative Addition

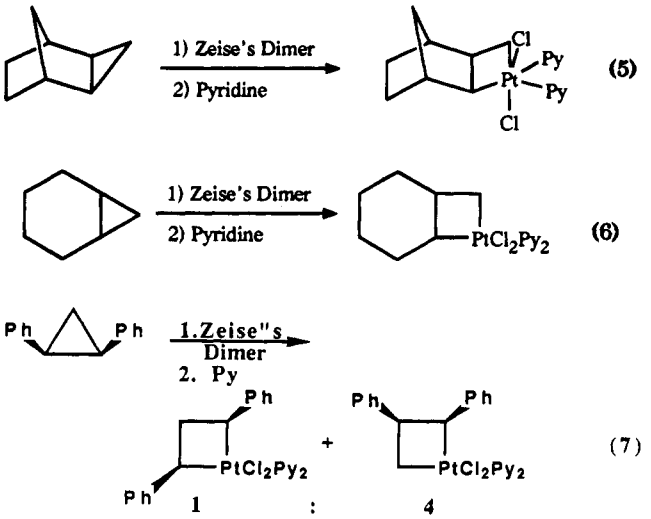
entry	complex	ref(s)	entry	complex	ref(s)
1[a]		61,72,73,94	12		91
2[b]		81,92	13		81
3		93	14		76
4		93	15		76
5		81	16		81
6		81	17		92
7		87	18[d]		88
8[c]		76	19		88
9		76	20		76,94
10		91	21		95
11		87	22		94

[a] Found as a mixture with the 1,3-disubstituted isomer, the 1,2-disubstituted isomer being predominant. [b] L = 4-Mepy, 2,5-diMepy, 3,6-diMepy, aniline, *p*-chloroaniline, DMAP, 2-methylpyrazine, en, bipy. [c] L = Py, en, (4-pyridyl)carbinol. [d] L = Py, bipy.

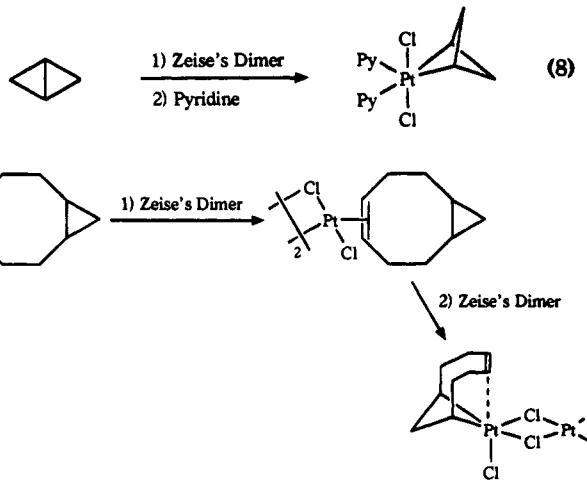
products were instead a mixture of olefins. Similar results were obtained from other cis-disubstituted cyclopropanes, and this led investigators to conclude that an unstable platina(IV)cyclobutane was formed en route to the observed olefinic products.[47,69,73] Some people erroneously concluded that Zeise's dimer did not react with cis-substituted systems. The origin of this enhanced reactivity with cis-disubstituted systems has not been definitively elaborated and is under investigation in the author's laboratory. It is clear that both steric and electronic factors are involved as expected. As you will see below many cis-disubstituted systems have been prepared. Those complexes derived from the norbornyl system are quite stable up to 50−80 °C. However, those derived from less sterically constrained systems such as cyclohexyl are considerably less stable and decompose to olefinic products at temperatures of 0 to 40 °C. The necessary requirement for decompositions is ligand loss to create a vacant coordination site to which hydride is transferred and decomposition commences. Thus, coordinative saturation prevents decomposition.

Likewise, as you will see in the reaction section, platinum(IV)cyclobutanes react by formation of cationic intermediates. Thus, α substituents provide for stabilized cationic intermediates which aid in complex reactivity.

Thus, a variety of cis-disubstituted platina(IV)-cyclobutanes have recently been synthesized, in high yield, from Zeise's dimer. Three examples are shown in eq 5,[87] 6,[88,89] and 7.[73,94] Additional complexes are illustrated in Table 4. For entries 7 and 11, a diendo



edge-bound structure was proposed as a stable complex.[87b] This has been shown to be incorrect. Two unique cis-1,3-disubstituted examples also exist in which platinum(II) is incorporated into the more highly substituted bond of the three-membered ring (eqs 8[90] and 9[66]). The final product of eq 9 is worthy



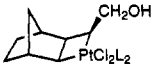
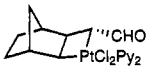
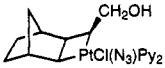
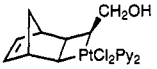
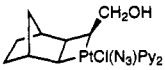
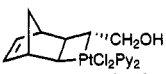
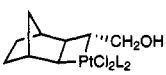
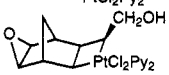
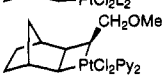
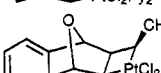
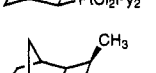
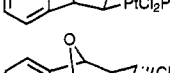
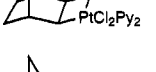
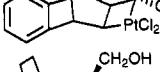
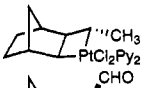
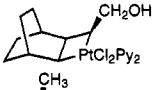
of additional comment. This is the first and only example of a platinum(IV) olefin complex. This is particularly interesting in light of the fact that high oxidation states are thought to not stabilize olefins and are often used to remove them from the coordination sphere. It also is significant with regard to the mechanism of oxidative addition of cyclopropane to Pt(II) which was discussed earlier in that it suggests that the olefin can remain on platinum during the reaction.

More highly substituted platinum(IV) complexes have been synthesized. For example, 1,1,2,2-tetramethylcyclopropane forms a relatively minute amount of platina(IV)cyclobutane upon reaction with Zeise's dimer, suggesting that steric effects also inhibit the oxidative addition of cyclopropane to Pt(II). When 1,1,2-trimethylcyclopropane is treated with Zeise's dimer, a tetrameric platina(IV)cyclobutane is formed. However, upon addition of pyridine, isomerization to a platinum–olefin species occurs and no monomer platina(IV)cyclobutane is observed. The bis-pyridine adduct of 1,1,2-trimethylplatina(IV)cyclobutane can be prepared, however, if pyridine is added to the corresponding tetramer at low temperatures (−40 °C).[69]

Recently, a variety of stable 1,2,3-trisubstituted platina(IV)cyclobutanes have been synthesized from the corresponding cyclopropanes and Zeise's dimer under mild conditions. Examples of these systems are listed in Table 5. Entries 8 and 9 were prepared by oxidation of entries 1 and 4, respectively. The rest were synthesized by oxidative addition methodology.

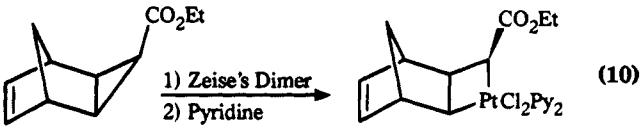
The oxidative addition of cyclopropane to Zeise's dimer is further limited since the ease of platina(IV)-cyclobutane formation rapidly decreases as the cyclopropane's substituents become more electron withdrawing.[62] In fact, when the cyclopropane is substituted with CO_2Me, COMe, or CN groups no direct platina(IV)cyclobutane formation is generally ob-

Table 5. 1,2,3-Trisubstituted Platina(IV)cyclobutanes via Oxidative Addition

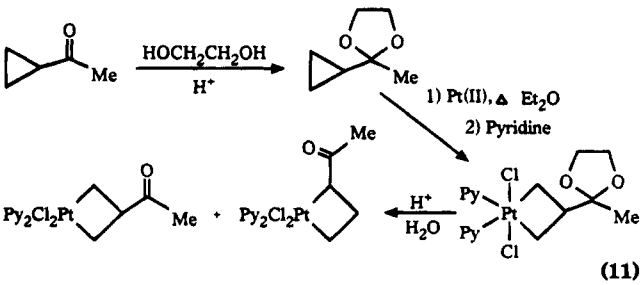
entry	complex	ref(s)	entry	complex	ref(s)
1[a]		81,96, 97	9		92
2		81	10		76
3		81	11		76
4[b]		96,97	12		76
5		81	13		76
6		92	14		76
7		92	15		81
8[b]		92,97	16		94

[a] L = Py, DMAP, bipy, en. [b] L = Py, bipy, en.

served with one exception (eq 10[76]). Apparently, the

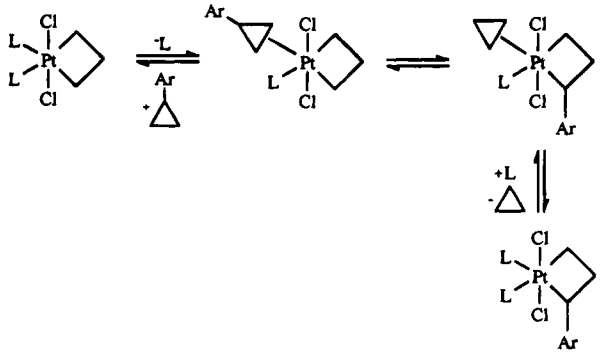


double bond of the norbornyl moiety contributes enough additional electron density to the electron-poor cyclopropane to allow insertion of the electrophilic Pt(II). These facts emphasize the concept that Pt(II) in this reaction is acting as an electrophile while the cyclopropyl moiety is playing the role as a nucleophile. To circumvent this limitation, an indirect methodology for preparing a platina(IV)cyclobutane bearing electron-withdrawing groups has been achieved recently (eq 11).[98]



The results of eq 11 address the problem of whether electron-withdrawing groups on the cyclopropane moiety retarded oxidative addition or allowed oxidative addition to an unstable platina(IV)cyclobutane which readily reductively eliminated. The facts are that oxidative addition appears to be retarded as the platina(IV)cyclobutane complexes (eq 11) are quite

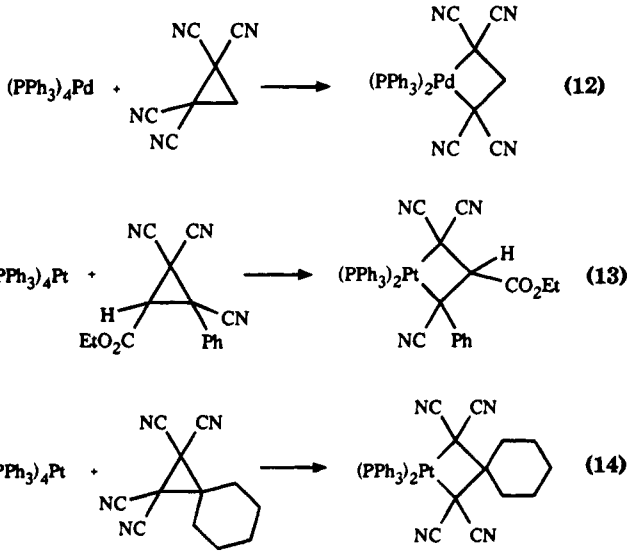
Scheme 2



stable to thermal decomposition. The same is true for entry 3 of Table 4. In this case, the complex is slow to form but is quite stable.

Another methodology for platina(IV)cyclobutane formation is shown in Scheme 2[99] This rather unique procedure has not been explored for a variety of substrates. Scheme 2 also illustrates the proposed mechanistic pathway for this displacement process.[64] Initial formation of an edge-bound cyclopropane–Pt complex is proposed as was previously inferred for platina(IV)cyclobutane formation (see Scheme 1).

Metal(0) as the Reagent. As demonstrated above, Pt(II) insertion into a C–C bond of cyclopropanes to form platina(IV)cyclobutanes is quite common. However, Pt(0) and other group eight transition metals also can be inserted into cyclopropanes to form their respective metallacyclobutanes. For example, Pd(0) and Pt(0) insert effectively into cyclopropanes bearing strong electron-withdrawing groups (eqs 12–14).[46,100–102] The 1,1,2,2 isomer was not observed. It



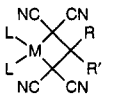
(12)

(13)

(14)

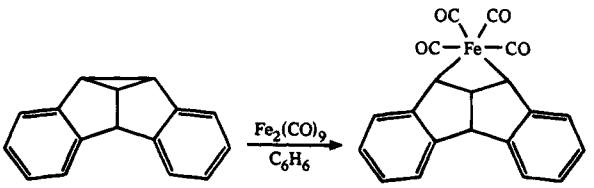
is important to contrast these results with those from the use of Pt(II). In the latter case, Pt(II) is acting as an electrophile, whereas in examples 12, 13 and 14, the metal is obviously a nucleophilic moiety. This explanation is further supported by the observation that $Pt(PPh_3)_4$ does not form a platina(II)cyclobutane upon reaction with the less electrophilic 1,2-dicyanocyclopropane.[102] Other pallada(II)- and platina(II)-cyclobutanes formed by oxidative addition methodology, in 20–80% yield, are listed in Table 6.

Table 6. Pallada(II)- and Platina(II)cyclobutanes via Oxidative Addition



entry	M	L	R	R′	ref(s)
1	Pd	PPh_3	Me	Me	102
2	Pd	PPh_2Me	Me	Me	102
3	Pt	PPh_3	H	H	100,102,103
4	Pt	PPh_3	Me	Me	102
5	Pt	PPh_3	H	Ph	101
6	Pt	PEt_3	H	H	102
7	Pt	PPh_2Me	H	H	102
8	Pt	PPh_2Me	Me	Me	102
9	Pt	$AsPh_3$	H	H	102
10	Pt	$AsPh_3$	Me	Me	102

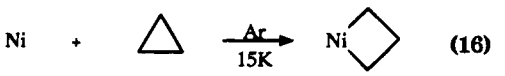
Dibenzosemibullvalene reacts with Fe(0) of diiron nonacarbonyl, according to eq 15, to form ferretane in 25% yield.[104] The rhodium analogue also has been



(15)

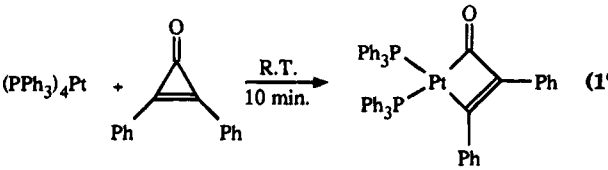
prepared, in 85% yield, from $Rh_2(CO)_4Cl_2$ and appears to be dimeric in nature.[105] The stability of these complexes may be attributed to the lack of β-elimination or C–C σ-bond rearrangement pathways.

Atomic nickel, when cocondensed in an argon matrix, can be inserted into cyclopropane to form an unligated nickela(II)cyclobutane (equation 16).[106]



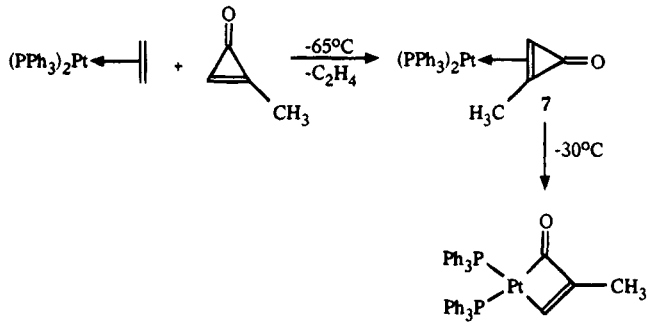
(16)

A second type of low-valent metallacyclobutane derivative, metallacyclobutenones, can be synthesized by metal insertion into cyclopropenones. Platina(II)cyclobutenones were the first complexes of this type to be prepared utilizing Pt(0) which readily inserts into the C–C single bond of the organic substrate (eqs 17a and 17b). Equation 17a reports a



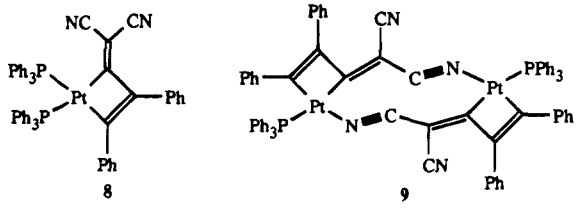
(17a)

direct synthesis of the diphenyl derivative which is formed in 60% yield.[107] In the reaction shown as eq 17b, an isolated intermediate **7** is initially formed, which upon further reaction at −30 °C yields the platina(II)cyclobutenone.[108] The possibility of trapping the platinum–olefin complex **7** seemingly depends on the ring substituents since the dimethyl and diphenyl derivatives formed the corresponding platina(II)cyclobutenones under the reaction conditions of eq 17a, but no olefinic complex was detected.

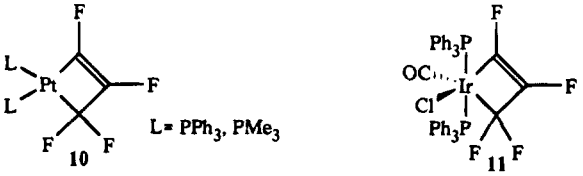


(17b)

Another metallacyclobutene of Pt(II) was prepared by treating 1,2-diphenyl-3-(dicyanomethylene)cyclopropene with bis(triphenylphosphine)(ethylene)-platinum to form the platina(II)cyclobutene monomer and dimer shown as **8** and **9**.[109]



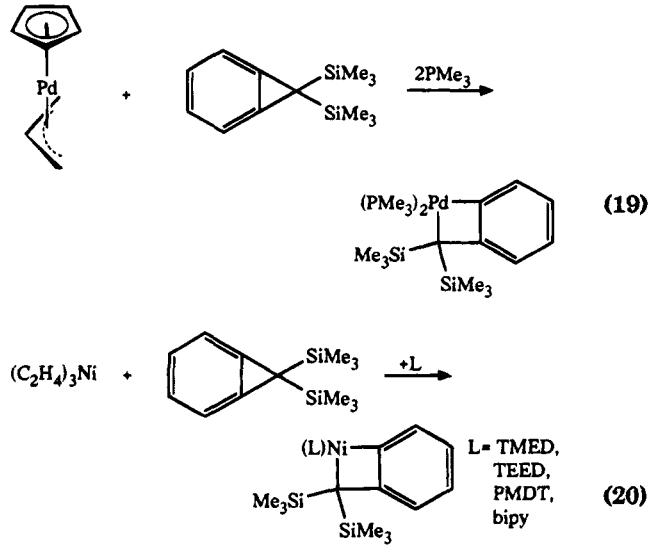
Tetrafluorinated cyclopropenes can also oxidatively add to the low-valent metal centers of Pt(0) and Ir(I) complexes to form tetrafluorinated platina(II)- and irida(III)cyclobutenes, respectively. Two examples are shown as **10**[110] and **11**.[111]



Metallacyclobutabenzene derivatives are a fourth class of low-valent metallacyclobutanes that can be prepared by the oxidative addition methodology. Nickela(II)cyclobutabenzene was the first of this class of compounds to be synthesized in this manner by treating cyclopropabenzene with $(PPh_3)_4Ni$ (eq 18).[112] Other nickel(0) sources that can be utilized effectively in this reaction include $(Et_3P)_2Ni(COD)$, $(n\text{-}Bu_3P)_2Ni(COD)$, or $Ni(C_2H_4)_3$ in TMED.

(18)

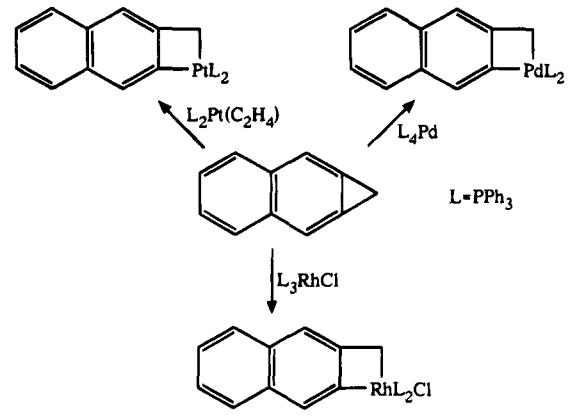
The synthesis described above also led to the preparation of bis(trimethylsilyl)-substituted palladа-(II)- and nickela(II)cyclobutabenzenes (eqs 19[113] and 20[114]). In eq 19, both the allyl and cyclopentadienyl ligands are proposed to be displaced and Pd(0) is inserted into one of the single bonds of the three-membered ring of 7,7-bis(trimethylsilyl)cyclopropabenzene. The nickelacycle is formed, in 61%–82% yield, with tris(ethylene)nickel and the cyclopropabenzene in the presence of a bidentate chelating ligand. When L = TMED, in this example, a ligand exchange reaction can occur to form the analogous



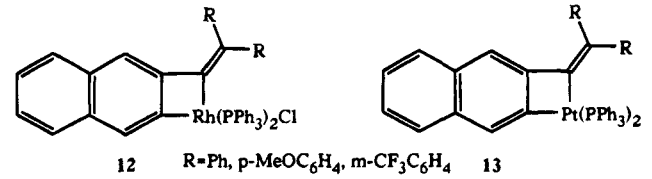
nickela(II)cyclobutabenzene compounds with phosphorous ligands PMe_3, dcpe, and dppe.

Further investigations of metal insertions into cycloproparenes has led to the preparation of metallacyclobutarenes of Rh(III) (74% yield), Pd(II), and Pt(II) (92% yield) as illustrated in Scheme 3.[115]

Scheme 3



Alkylidene-1-rhoda(III)- and -platina(II)cyclobutarenes **12** and **13**, respectively, also have been prepared from $(PPh_3)_3RhCl$ and $(PPh_3)_4Pt$, respectively (60%–85% yield).[116]

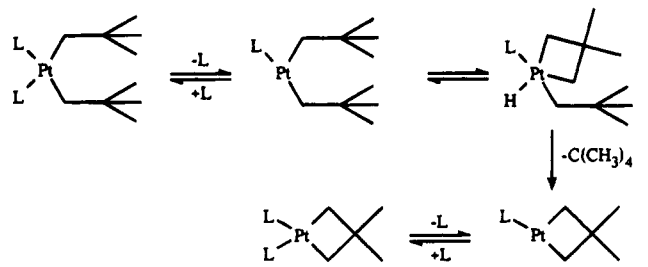


12 R=Ph, p-$MeOC_6H_4$, m-$CF_3C_6H_4$ 13

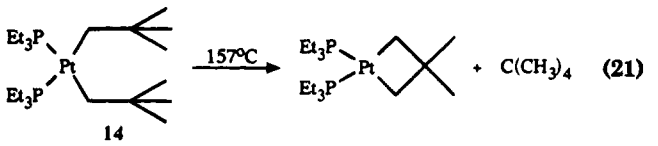
B. Carbon–Hydrogen Bond Cleavage

The intramolecular oxidative addition of C–H bonds to a central metal atom, commonly referred to as a cyclometalation reaction, can form an assortment of metallacyclic complexes including metallacyclobutanes, -butanones, and -butabenzenes. The most thoroughly studied example of this methodology involves the thermal decomposition of dineopentylbis(triethylphosphine)platinum(II) to form bis(trieth-

Scheme 4

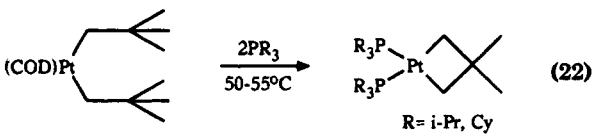


ylphosphine)-2,2-dimethylplatina(II)cyclobutane in70% yield (eq 21).[117] In this reaction, an unactivated γ



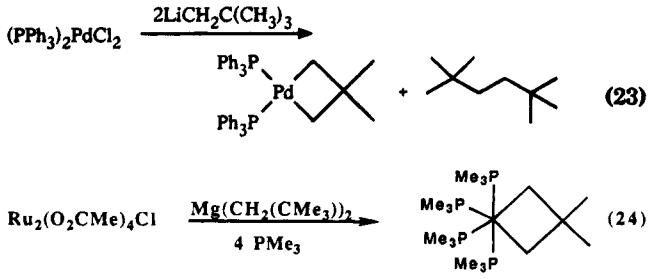
C−H bond is cleaved by the platinum moiety under vigorous conditions to form the platina(II)cyclobutane. The mechanism has been investigated and is outlined in Scheme 4.[117−120] Studies have indicated relief of steric congestion in the dineopentylplatinum complex as the driving force of the reaction.

Compound **14** was prepared in good yield by treating (1,5-COD)$PtCl_2$ with neopentylmagnesium bromide followed by addition of triethylphosphine. The corresponding reactions of (1,5-COD)Pt[$CH_2C(CH_3)_3$]$_2$ with triisopropylphosphine and tricyclohexylphosphine do not form the expected analogues to **14**, however, but lead directly to platina(IV)cyclobutane formation in 19% and 17% yields, respectively (eq 22).[121] The difference in products in these latter

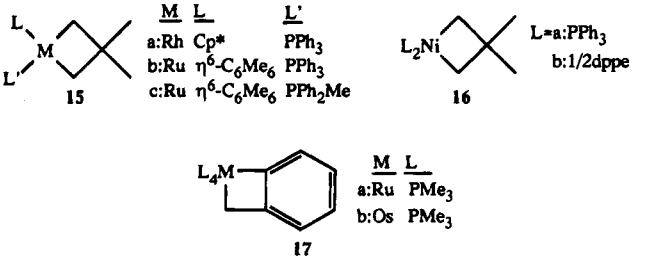


reactions is presumably due to the increased steric bulk of triisopropyl- and tricyclohexylphosphine, relative to triethylphosphine, making formation of a stable square planar Pt(II) dineopentyl complex less likely.

The mechanism shown in Scheme 4 for 2,2-dimethylplatina(II)cyclobutane formation is also invoked in the preparation of the 2,2-dimethylmetallacyclobutanes formed in eqs 23[122] and 24.[123] Other

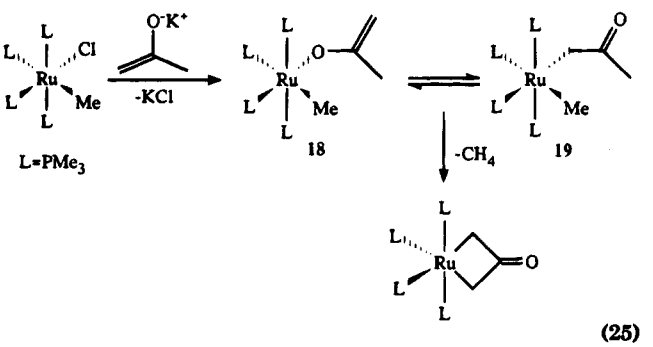


metallacyclobutane and -butabenzene complexes that have been prepared by this methodology, in yields ranging from 12% to 70%, are shown as **15a−c**,[124−127] **16a** and **b**,[122] and **17a**[128,129] and **b**.[130]



Irida(III)cyclobutane, -butanone, and -butabenzene have been prepared via cyclometalation reactions according to Scheme 5.[128,131] Each reaction shown in Scheme 5 involves the intramolecular insertion of iridium(I) into a γ C−H bond of the alkyl or aryl moiety. The cyclometalation mechanism of the iridium examples differs slightly, however, from the cyclometalation pathway outlined in Scheme 4, since no sacrificial alkyl ligand is present to reductively eliminate with the abstracted hydrogen. Subsequent mechanistic studies revealed that ligand dissociation does not occur prior to oxidative addition of the C−H bond to iridium, suggesting direct oxidative addition of the C−H bond to a square planar monoalkyl (or aryl) iridium intermediate.[132]

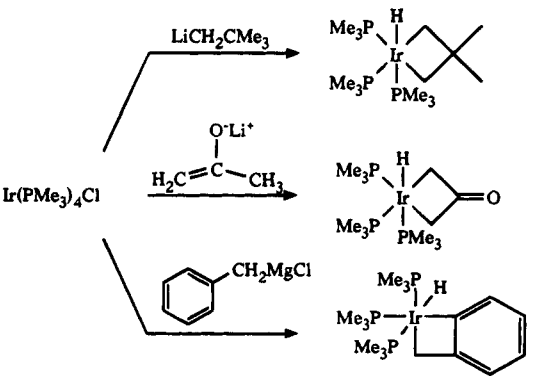
An analogous product to the irida(III)cyclobutanone formed in Scheme 5 can be prepared for ruthenium as illustrated in eq 25.[133] An equilibrium



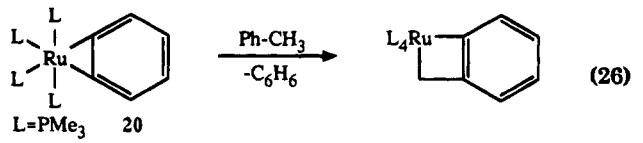
(25)

is first established between the ruthenium enolate complexes **18** and **19** which exist in both the C- and O-bound forms in a 70:30 ratio. Thermolysis of this mixture leads to loss of methane and formation of the ruthena(II)cyclobutanone product in 74% yield as determined by ^1H NMR spectroscopy at −20 °C. This metallacyclobutanone is extremely unstable but was isolated and characterized at low temperatures.

Scheme 5



A ruthena(II)cyclobutabenzene results from the reaction of a ruthenium–benzyne complex with toluene under the conditions described in eq 26.[134] It has not been determined whether the metallacyclic product results from initial reaction of **20** with the ortho position of toluene followed by metalation of the benzylic methyl group or by initial reaction with the benzylic C–H bond followed by orthometalation.

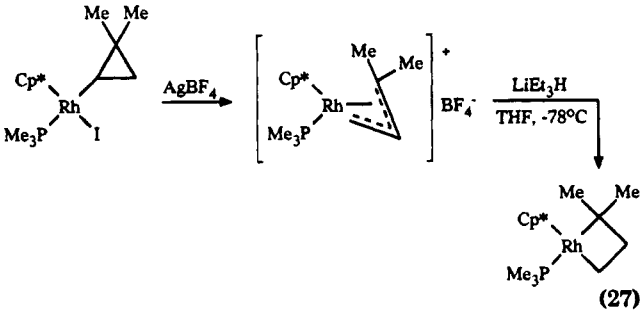


(26)

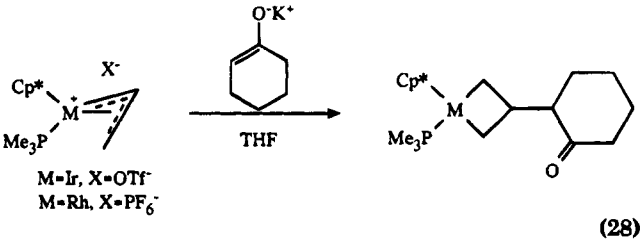
C. Nucleophilic Addition to Metal–π-Allyl Complexes Methodology

Nucleophilic addition to the central carbon of π-allyl–transition metal complexes can form two types of metallacyclobutane products. Simple metallacyclobutanes can be synthesized from an isolated metal–π-allyl complex, and a tricyclic ring closure product, containing a metallacyclobutane moiety, results from nucleophilic attack on a desired metal–π-allyl intermediate.

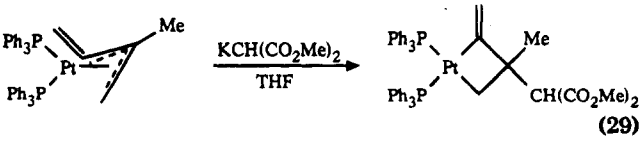
Four examples of metallacyclobutanes prepared by this methodology are shown in eqs 27,[135] 28,[136,137] 29,[138] and 30.[139] Other metallacyclobutanes synthesized by this methodology are exhibited in Table 7. That the nucleophile attacks at the central carbon, rather than the terminal carbon, of the π-allyl system is unusual and is reportedly the result of frontier orbital control as well as charge control.[140–142] In addition, the reactions shown in eqs 29 and 30 indicate that β-alkyl substitution on the allylic group does not prevent nucleophilic attack. It is important to note that the rhodium and iridium π-allyl complexes are +3 oxidation state while that for platinum is +2.



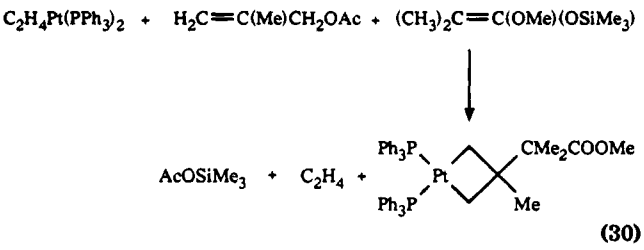
(27)



(28)

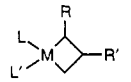


(29)



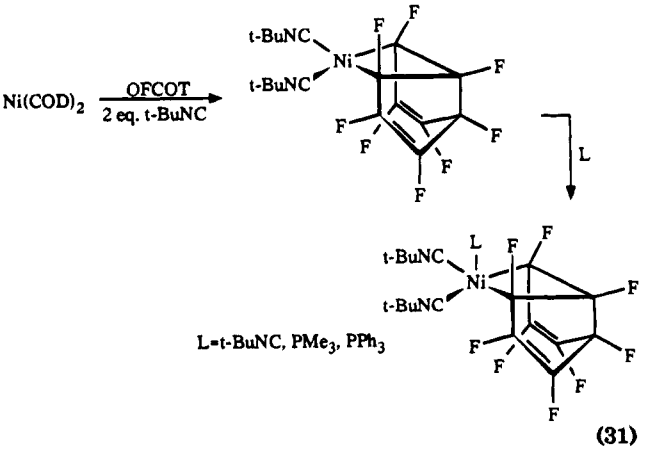
(30)

Table 7. Rhoda(III)-, Irida(III), and Platina(II)cyclobutanes via Nucleophilic Addition to Metal π-Allyl Complexes

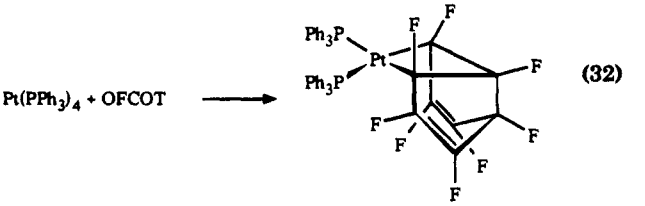


M	L	L′	R	R′ (Nu)	ref
Rh	Cp*	PMe_3	H	H	135
Rh	Cp	PMe_3	Me	H	143
Rh	Cp	$P(i\text{-}Pr)_3$	Me	H	144
Rh	Cp	$P(i\text{-}Pr)_3$	H	$CHCl_2$	144
Rh	Cp	PMe_3	Me	Me	143
Rh	Cp	$P(i\text{-}Pr)_3$	Me	Me	144
Rh	Cp	$P(i\text{-}Pr)_3$	Me	$CHCl_2$	143
Rh	Cp	$P(i\text{-}Pr)_3$	Me	CCl_3	143
Rh	Cp*	PMe_3	H	CHMeC(O)Ph	136
Ir	Cp*	PMe_3	H	H	145
Ir	Cp*	C_2H_4	H	H	142
Ir	Cp*	C_2Ph_2	H	H	146
Ir	Cp*	PMe_3	H	Me	145
Ir	Cp*	CO	H	$CH(CO_2Me)_2$	147
Ir	Cp*	CO	H	CN	147
Ir	Cp*	CO	H	CHMeC(O)Ph	147
Ir	Cp*	PMe_3	H	CHMeC(O)Ph	136
Ir	Cp*	C_2H_4	H	CHMeC(O)Ph	142
Ir	Cp*	C_2Ph_2	H	CHMeC(O)Ph	146
Ir	Cp*	C_2Me_2	H	CHMeC(O)Ph	146
Pt	PPh_3	PPh_3	H	CMe_2CO_2Me	139
Pt	$P(C_6H_{11})_3$	$P(C_6H_{11})_3$	H	CMe_2CO_2Me	139
Pt	PPh_3	PPh_3	Me	CMe_2CO_2Me	139
Pt	½(dppe)		H	$CHMeCO_2Me$	139

Three examples of the second type of metallacyclobutane product formed by nucleophilic attack of an internal carbanion on the central carbon of a proposed π-allyl metal intermediate are shown in Scheme 6[148] and eqs 31[149,150] and 32.[151] In each

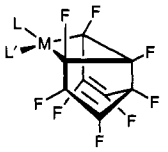


(31)



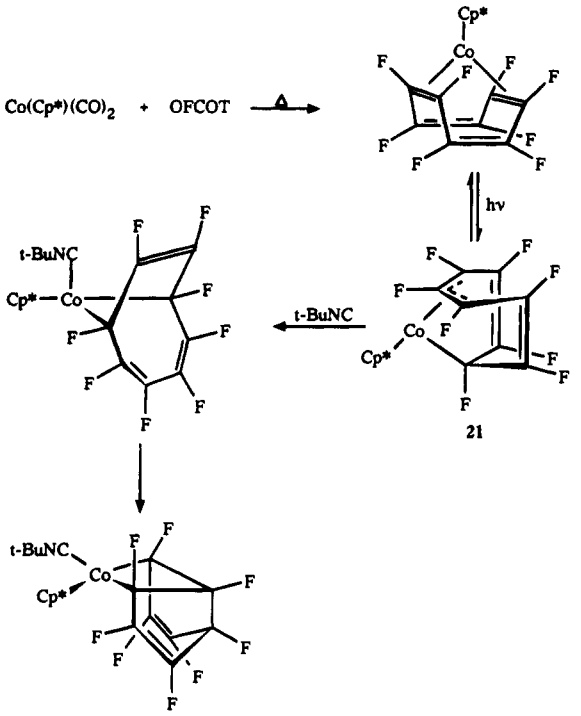
(32)

Table 8. Cobalta(II)-, Rhoda(III)-, Pallada(II)- and Platina(II)cyclobutanes via Transannular Ring Closure Reactions



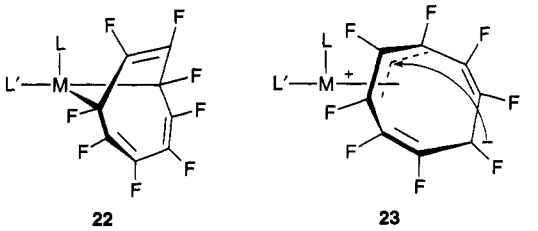
M	L	L'	ref
Co	CO	Cp*	151
Rh	*t*-BuNC	Cp*	148
Rh	PMe_3	Cp*	148
Rh	*t*-BuNC	indenyl	152
Pd	PPh_3	PPh_3	149
Pd	*t*-BuNC	*t*-BuNC	149
Pt	$PPhMe_2$	$PPhMe_2$	151
Pt	PPh_2Me	PPh_2Me	151
Pt	$AsPh_3$	$AsPh_3$	149
Pt	*t*-BuNC	*t*-BuNC	149

Scheme 6



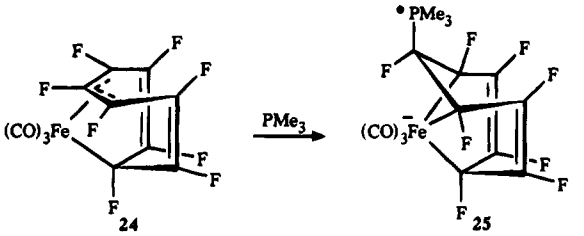
example, a metal complex is treated with octafluorocyclooctatetraene (OFCOT) under varying conditions, to generate a transannular ring closure product containing a metallacyclobutane moiety. Other metallacyclobutane products resulting from this methodology are shown in Table 8.

Although the various metal complexes utilized in the reactions in Scheme 6, eqs 31 and 32, and to generate the products shown in Table 8 require different reaction conditions to arrive at the observed ring closure product, a common metallacyclopentane intermediate **22** is suggested for each reaction and actually was isolated and characterized in the cobalt and rhodium examples. It is this intermediate that can be transformed into a zwitterionic species **23** containing a π-allyl–metal moiety. Attack of the negatively charged carbon on the central carbon of the allyl leads to the observed metallacyclobutane products.[152]



22 **23**

A similar reaction of Fe(0) with OFCOT leads to a different type of metallacyclobutane product as external nucleophilic attack at the central carbon of an iron–π-allyl complex occurs. In this case, $Fe_2(CO)_9$ is treated with OFCOT resulting in the formation of π-allylic iron complex **24** (a similar structure to **21** in Scheme 6). Subsequent addition of PMe_3 leads to formation of the trialkyltricarbonyliron(IV) complex **25** presumably via attack of PMe_3 on the central π-allylic carbon (eq 33).[153] Further, treatment of **24** with the anionic nucleophile $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ adds an additional fluorine at the center carbon of the allylic moiety to form the analogous anionic nonafluoro complex.

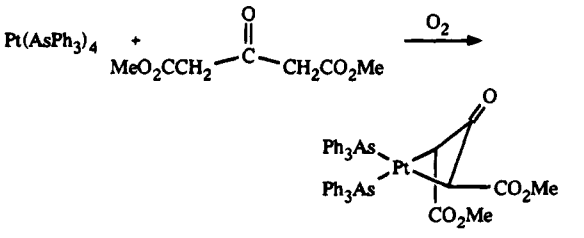


(33)

D. Other Methodologies

The synthesis of metallacyclobutane derivatives is not limited, however, to the previously described methodologies. A number of other procedures have also proven effective.

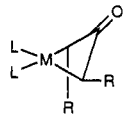
Metallacyclobutanones can be prepared by three different methodologies in addition to the cyclometalation reactions described previously. Reaction of Pt(0) and Pd(0) species, $Pt(PR_3)_4$, $Pt(AsPh_3)_4$, $Pt(CO_3)(PR_3)_2$, *cis*-$Pt(OCOPh)_2$, *cis*-$PtCl_2(PPh_3)$, $Pd(PR_3)_2$, or $Pd_2(dba)_2$, with esters of 3-oxopentanedioic acid or 2,4,6-heptatrione, under various reaction conditions, produces pallada(II)- and platina(II)cyclobutanones, in high yield. One example of this methodology is shown in eq 34.[154] Other examples of metallacyclobutanones synthesized from the metal species and reagents discussed above are listed in Table 9. In each case, one substituent on the metallacyclobutanone ring occupies an equatorial position, while the other is found to be axial as shown.



(34)

The silyl compound 3-chloro-1-(trimethylsilyl)propan-2-one can be utilized as a reagent to generate osmia(II)- and irida(III)cyclobutanones, as well as the

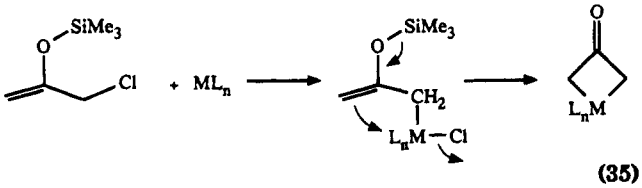
Table 9. Pallada(II)- and Platina(II)cyclobutanones via Reaction with Acidic Substrates



M	L	R	ref(s)
Pd	PPh_3	CO_2Me	155–158
Pd	PPh_3	CO_2Et	157,158
Pd	PPh_2Me	CO_2Me	156,157
Pd	$PPhMe_2$	CO_2Me	156,157
Pd	PEt_3	CO_2Me	157
Pd	$AsPh_3$	CO_2Me	156,157
Pd	$AsPh_3$	CO_2Et	157
Pd	$^1/_2$(bipy)	CO_2Me	156–158
Pd	$^1/_2$(bipy)	CO_2Et	157
Pd	$^1/_2$(bipy)	CO_2-*n*-Pr	157
Pt	PPh_3	CO_2Me	154,155,158[b]
Pt	PPh_3	CO_2Et	154
Pt	PPh_3	CO_2-*n*-Pr	154
Pt	PPh_3	COMe	159,160
Pt	PPh_3	CO_2Et,CO_2-*n*-Pr[a]	159
Pt	PPh_2Me	CO_2Me	154,155,158[b]
Pt	$PPhMe_2$	CO_2Me	154,155,158[b]
Pt	$^1/_2$(dppe)	CO_2Me	154,158,159
Pt	$AsPh_3$	CO_2Et	154
Pt	$AsPh_3$	CO_2-*n*-Pr	154
Pt	$AsPh_3$	COMe	159,160

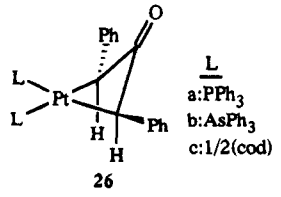
[a] Each group occupies one R position. [b] Also found in ref 159.

Pt(II) analogue, according to Scheme 7.[161] The reaction is suggested to proceed from the silylenol ether rather than the respective ketone and to follow the oxidative addition pathway shown in eq 35.[162]



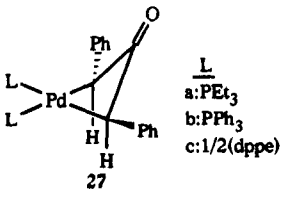
(35)

Metallacyclobutanones of Pt(II) **26a–c** and Pd(II) **27a–c** bearing phenyl substituents can be synthesized from the dianion of 1,3-diphenylacetone in yields ranging from 42% to 93%.[163] In contrast to the substituents of the metallacyclobutanones of Table 9, both of the phenyl substituents on **26a–c** and **27a–c** adopt equatorial positions. This novel substi-



26

L
a:PPh_3
b:$AsPh_3$
c:1/2(cod)



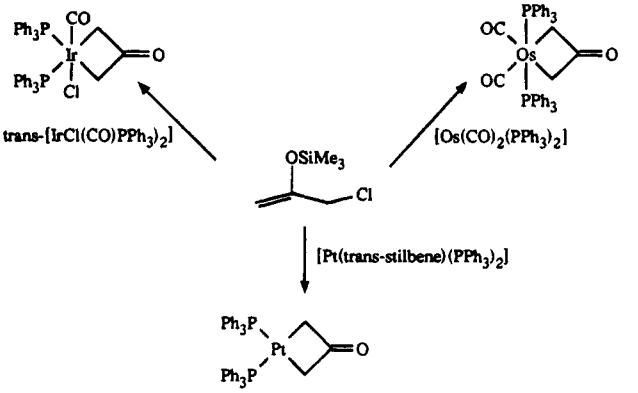
27

L
a:PEt_3
b:PPh_3
c:1/2(dppe)

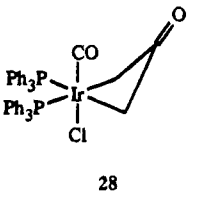
tution is best explained by the increased conjugation that can be achieved between the phenyl groups and the π-system of the oxodimethylene ligand when an equatorial orientation is adopted or from the conformational preference of the lithium dianion percursor. The latter seems more likely.

Characterization of the metallacyclobutanones prepared by the three methodologies described above has revealed a highly puckered ring system. The degree of puckering ranges from 41° in **28**[161] to 56.7° in **29**[163]

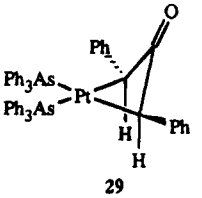
Scheme 7



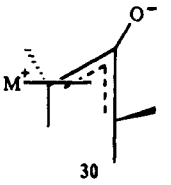
and is believed to result from a transannular attraction between the metal and the β-carbonyl group. In fact, the bonding description of these metallacycles should include considerable contribution from an η^3-oxodimethylenemethane structure **30**, and in the most highly puckered cases is more logically suggested as such. The amount of π-allylic contribution in these systems is related to variations in the metal, the ligands, and the ring substituents.



28

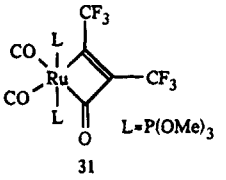


29



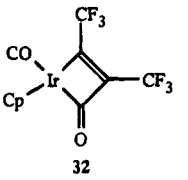
30

Metallacyclobutenones **31–33** can be synthesized from the reaction of alkynes bearing strong electron-withdrawing CF_3 groups with *trans*-$(CO)_3(P(OMe)_3)_2$-Ru, $Cp(CO)_2Ir$, and $Cp^*(CO)_2Ir$, respectively.[164–166]

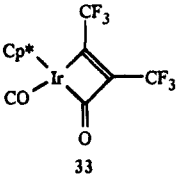


31

L=$P(OMe)_3$

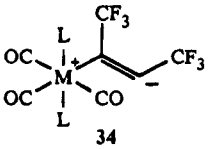


32



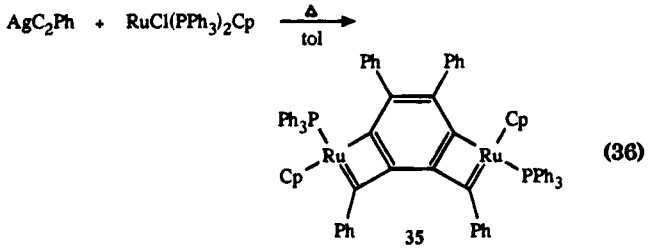
33

The reaction pathway for the synthesis of **31** suggests initial formation of an ionic intermediate **34** followed by nucleophilic attack by the carbanion on the coordinated carbon monoxide to give the ruthena(II)-cyclobutene product.



34

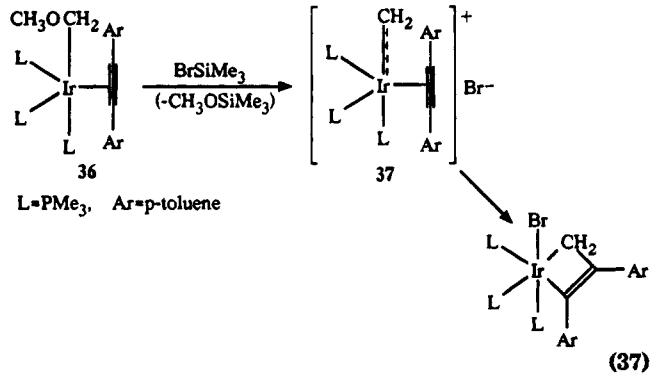
The unusual tetramerization of alkynes is proposed for the formation of the diruthenadicyclobuta[*a*,*c*]-benzene complex **35**, in 24% yield, from the reaction of AgC_2Ph and $RuCl(PPh_3)_2$ as shown in eq 36.[167] Also isolated in small yields from this reaction was a diruthenapentacyclic pentalene system. The formation of both products is attributed to the oligomerization of phenylacetylide units on ruthenium. The proposed pathway for the formation of **35** is shown



(36)

in Scheme 8. Initial formation of two ruthenium σ-phenylacetylide complexes is followed by oxidative coupling to form the ruthenium divinylidene complex. Further coupling with 1,4-diphenylbuta-1,3-diyne, which also is formed by oxidative coupling of phenylacetylide units, leads to **35** as shown.

Another methodology incorporating alkynes involves conversion of a (methoxymethyl)iridium(I) acetylene complex **36** to an irida(III)cyclobutene presumably by the [2 + 2] cycloaddition pathway shown in eq 37.[168] The C–O bond of the methoxy

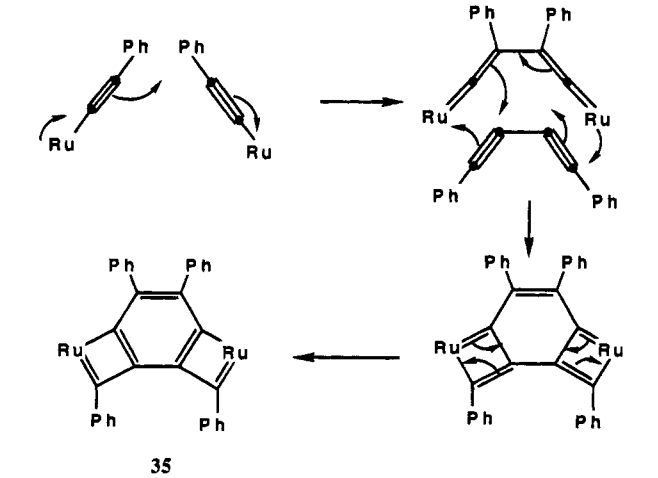


(37)

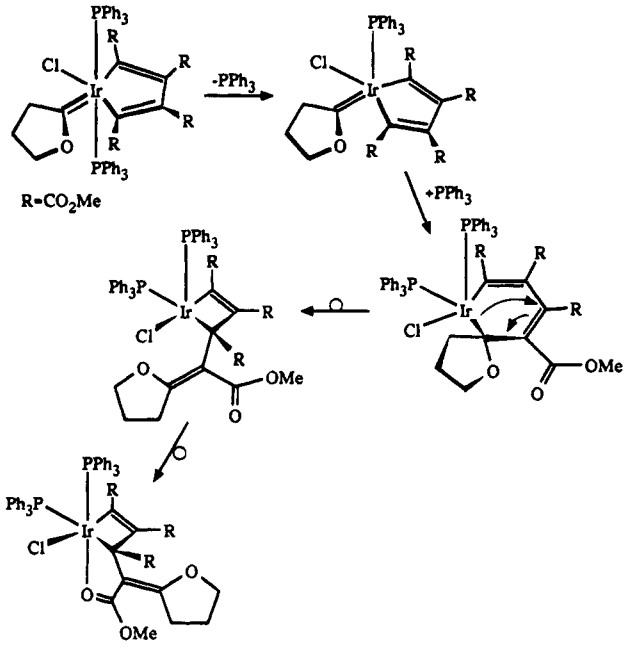
group is easily cleaved by the electrophilic reagent bromotrimethylsilane to form the suggested iridium–carbene intermediate **37**. The iridium–carbene then can undergo a [2 + 2] cycloaddition to the π-bound acetylene to form the observed metallacyclobutene product in 66% yield.

Also an irida(III)cyclobutene is formed from the novel rearrangement of an irida(III)cyclopentadiene–carbene complex according to Scheme 9.[169] This conversion reportedly proceeds via carbene ligand insertion into the α-carbon–metal bond of the irida(III)cyclopentadiene. A 1,3-shift of iridium and co-

Scheme 8

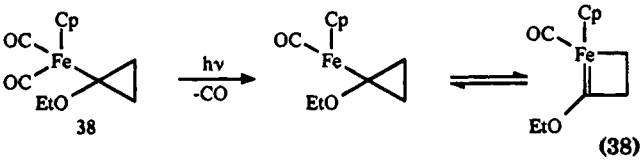


Scheme 9



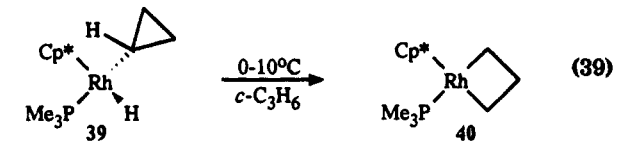
ordination of the ester carbonyl led to the irida(III)-cyclobutene product.

A highly unstable 1-ferracyclobutene reportedly has been synthesized by the photolysis of a σ-cyclopropyl complex of dicarbonyl(η^5-cyclopentadienyl)iron **38** followed by rapid low-temperature (−50 °C) flash chromatography over silica gel.[170,171] As eq 38 illustrates, the α-ethoxy cyclopropane complex **38** initially loses CO to give a 16-electron intermediate that subsequently undergoes rearrangement to yield the unusual cyclic carbene complex, 1-ferracyclobutene. It is significant to note the analogy of this reaction with the cyclopropyl carbinyl cation rearrangement.



(38)

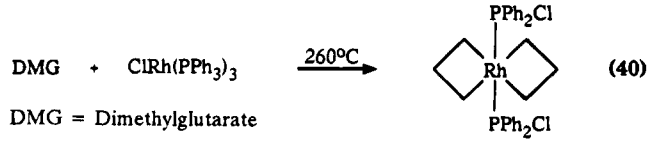
A similar intramolecular rearrangement of a cyclopropyl σ complex of rhodium hydride **39** to form a rhoda(III)cyclobutane has been suggested for the reaction shown in equation 39.[135,172] Kinetic and ^{13}C-



(39)

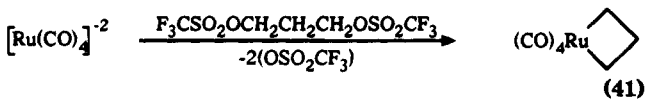
labeling studies have indicated that the cyclopropyl moiety and the rhodium remain intact during conversion of **39** to **40**, and that rearrangement occurs by regiospecific insertion of Rh(III) into an α C–C bond of the cyclopropyl ring thus supporting an intramolecular rearrangement pathway. Hydride transfer follows.

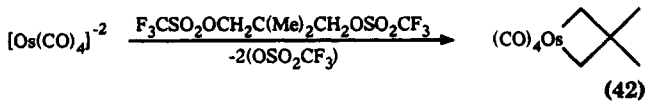
A unique rhodacyclobutane (a spirorhodacycle) reportedly is produced in the reaction shown in eq 40.[173] The pyrolysis of dimethyl glutarate, DMG, with Wilkinson's salt, $ClRh(PPh_3)_3$, produces a large number of products. Six rhodium-containing compounds



were isolated, one being the rhodacyclobutane shown. Initial oxidative addition into the C−O bond of DMG, followed by additional reactions accounts for the formation of the Rh compounds. However, the additional reactions necessary to form the rhoda(IV)-cyclobutane are not obvious. The oxidation state of rhodium in the spirorhodacycle is unusual.

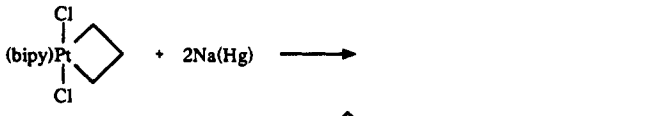
Ruthena(II)- and osmia(II)cyclobutanes can be synthesized by nucleophilic elimination cycloaddition on the alkanediyl bis(trifluoromethanesulfonate) with the divalent anions $[M(CO)_4]^{-2}$ according to eqs 41 and 42.[174] An analogous unsubstituted osmia(II)-

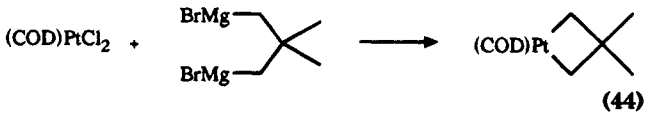




cyclobutane also can be synthesized by the reaction shown in eq 41 and is found to be considerably more thermally stable than the ruthenium homologue.

Both the sodium amalgam reduction (or the less convenient cathodic reduction) of platina(IV)cyclobutane, eq 43,[175,176] and the reaction of a 1,3-diGrignard reagent with a Pt(II) species, eq 44,[177] can be used to prepare platina(II)cyclobutanes in high yield. These

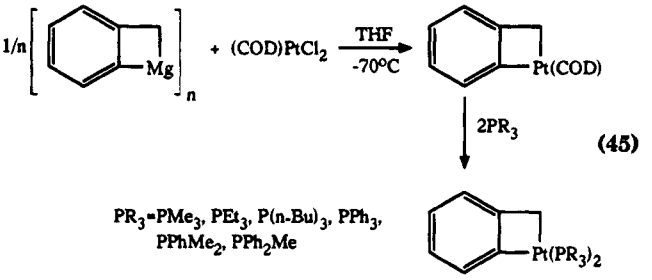




methodologies are useful in preparing platina(II)-cyclobutanes without the electronegative substituents required for Pt(0) insertion into cyclopropanes (see eqs 12 and 13). Both the bipyridyl and COD ligands are labile and can be displaced readily by monodentate ligands to form platina(II)cyclobutanes with L = PPh_3, PMe_3, PEt_3, P(*t*-Bu)$_3$, and *t*-BuNC.

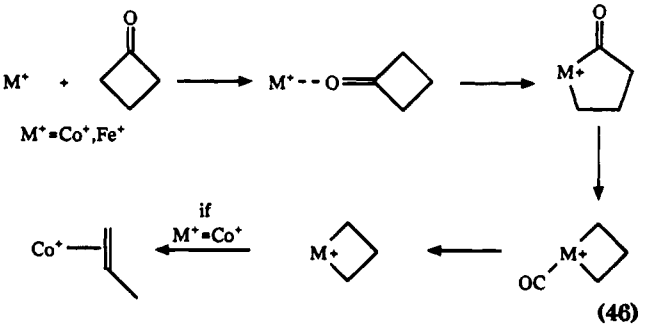
In the reaction shown as eq 45, oligomeric 1,2-dihydromagnesacyclobutabenzene is employed as the 1,3-diGrignard equivalent to generate a platina(II)-cyclobutabenzene via transmetalation.[178] Again, the labile COD ligand is replaced by a variety of monodentate phosphorous ligands as shown.

A platina(IV)cyclobutane can be formed in 94% yield by reacting diazofluorene with Zeise's pyridine monomer according to Scheme 10.[70] The pathway for this transformation which involves ethylene insertion suggests initial formation of a ylide intermediate



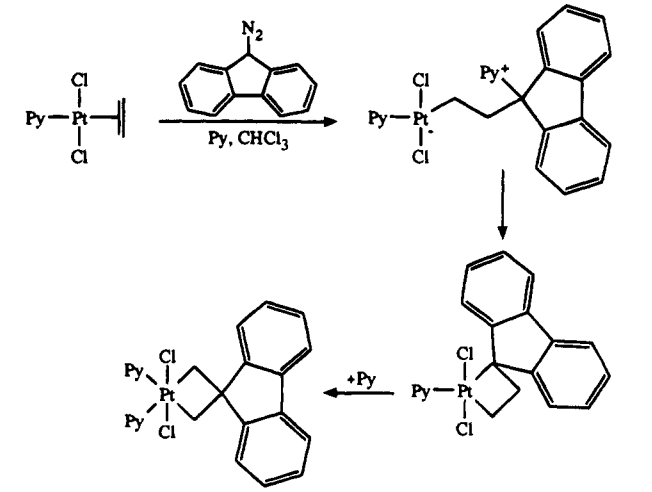
which subsequently cyclizes to form an α-substituted platina(IV)cyclobutane. A Puddephatt-type rearrangement and addition of pyridine leads to the observed product. The ylide intermediate was observed by NMR spectroscopy from reactions run at low temperatures (−40 to 0 °C) and was found to form the platina(IV)cyclobutane upon warming. The α-substituted cyclic intermediate was not observed but ample precedent is reported for the rearrangement of α-substituted platina(IV)cyclobutanes to their β-substituted counterparts.

Metallacyclobutane ions can be formed in the gas phase with Fe^+ and Co^+ according to eq 46.[179,180] The



ferra(III)cyclobutane ion formed is stable, whereas the corresponding cobalta(III)cyclobutane ion has been found to isomerize to a π-complexed propene product.

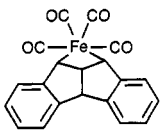
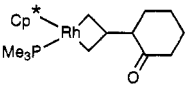
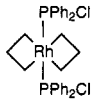
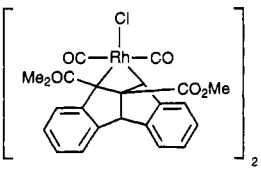
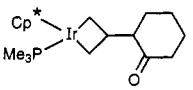
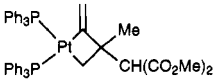
Scheme 10



III. Characterization of Metallacyclobutane Derivatives

The use of ^1H and ^{13}C NMR spectroscopy along with X-ray crystallographic analysis has aided the characterization of metallacyclobutane derivatives

Table 10. ^{1}H NMR Chemical Shift Data (ppm) of Ferra(II)-, Ruthena(II)-, Osmia(II)-, Rhoda(III)-, Irida(III)-, Nickela(II)-, Pallada(II)- and Platina(II)cyclobutanes

complex	H^α	H^β	ref(s)
	3.04	4.55	104
$(\eta^6\text{-}C_6H_6)(PPH_3)Ru[CH_2CMe_2CH_2]$	0.22,0.53		127
$(\eta^6\text{-}C_6H_6)(PPh_2Me)Ru[CH_2CMe_2CH_2]$	0.26,0.41		127
$(CO)_4Os[CH_2CH_2CH_2]$	0.63	3.73	174
$(Cp^*)(PMe_3)Rh[CH_2CH_2CH_2]$	0.20,0.38	3.20,3.48	172
$(Cp^*)(PMe_3)Rh[CH_2CMe_2CH_2]$	0.23,0.32		172
$(Cp^*)(PMe_3)Rh[CMe_2CH_2CH_2]$	0.53,0.81	2.52,3.41	172
$(Cp^*)(PPh_3)Rh[CH_2CMe_2CH_2]$	0.41		124,125
$(Cp)(P(i\text{-}Pr_3))Rh[CHMeCH_2CH_2]$	2.06[a]	2.55,3.71	144
	0.27,0.98[b]		
	0.50−0.60	2.85	137
	−0.08 to 0.38		
	1.00	1.3	173
	5.70		105
$(Cp^*)(C_2H_4)Ir[CH_2CH_2CH_2]$	0.96	2.80,4.14	142
$(AsMe_3)_3HIr[CH_2CMe_2CH_2]$	0.92		131
$(Cp^*)(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[c]	0.48,1.12	2.34	137
$(Cp^*)(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[d]	0.35,1.45	2.57	142
$(Cp^*)(PMe_3)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[d]	0.93,1.05[e]	2.84	137
	0.42−0.52[f]		
	0.92,0.96[e]	2.79	137
	0.32,0.55[f]		
$(PPh_3)_2Ni[CH_2CMe_2CH_2]$	1.07		122
$(dppe)Ni[CH_2CMe_2CH_2]$	1.14		122
$(PPh_3)_2Pd[CH_2CMe_2CH_2]$	0.85		122
$(PPh_3)_2Pt[CH_2CH(CMe_2COOMe)CH_2]$	0.10,0.44[g]	3.02	139
$(P(C_6H_{11})_3)_2Pt[CH_2CH(CMe_2COOMe)CH_2]$	−0.01,0.66[h]	2.84	139
$(dppe)Pt[CH_2CH(CHMeCOOMe)CH_2]$	−0.04,−0.20,0.74[i]	3.04	139
$(PPh_3)_2Pt[CH_2C(Me)(CMe_2COOMe)CH_2]$	0.11,0.56[j]		139
$(PPh_3)_2Pt[CH(Me)CH(CMe_2COOMe)CH_2]$[i]	0.00,0.34[k]	3.06	139
	0.60[k]		
	0.95,1.66		138

[a] RhC*H*Me. [b] RhCH_2. [c] Ring substituent syn to Cp*. [d] Ring substituent anti to Cp*. [e] H^α trans to Cp*. [f] H^α trans to PMe_3. [g] $^2J_{Pt-H}$ = 80, 84. [h] $^2J_{Pt-H}$ = 70, 78. [i] $^2J_{Pt-H}$ = 78, 81. [j] $^2J_{Pt-H}$ = 83. [k] Ring substituents trans, $^2J_{Pt-H}$ = 80, 90, δ = 0.60 ppm C*H*Me; no $^2J_{Pt-H}$ data for this proton.

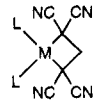
tremendously. This section provides an extensive ^{1}H NMR, ^{13}C NMR, and X-ray crystallography database for those metallacyclobutane derivatives for which this information has been reported.

A. ^{1}H NMR Spectroscopy

Tables 10−23 display the reported ^{1}H NMR chemical shift (ppm) and metal−proton coupling constant (Hz) data (where applicable) for metallacyclobutane complexes. The effect of the metal on the proton chemical shift in these systems is evident when comparing the data for analogous rhoda(III)- and irida(III)cyclobutanes found in Table 10. The chemical shift of the α protons in the irida(III)cyclobutanes are found further downfield consistently. A similar effect is observed in Table 11 when comparing the β-proton chemical shifts of analogous pallada(II)- and platina(II)cyclobutanes. The decreased shielding caused by Ir(III) and Pt(II) is attributable to their increased ability to accept electron density from the carbon ring system.

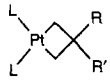
The data for the platina(II)cyclobutanes in Table 12 illustrate the substantial influence that the coordinated ligands have on the proton chemical shifts.

Table 11. ^{1}H NMR Chemical Shift Data (ppm) of Pallada(II)- and Platina(II)cyclobutanes



M	L	H^β ($^3J_{Pt-H}$)	ref
Pd	PPh_3	3.96	102
Pd	PPh_2Me	4.0	102
Pt	PEt_3	4.34 (28)	102
Pt	PPh_3	4.38 (38)	102
Pt	PPh_2Me	4.40 (30)	102
Pt	$PPhMe_2$	4.49 (26)	102
Pt	$AsPh_3$	4.39 (44)	102

Table 12. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant Data (Hz) of Platina(II)cyclobutanes



L	R	R′	H^α ($^2J_{Pt-H}$)	H^β ($^3J_{Pt-H}$)	Me ($^4J_{Pt-H}$)	ref(s)
1/2(cod)	Me	Me	1.19 (108.8)		1.40 (2.7)	177
1/2(bpy)	H	H	1.29 (115)	3.32 (110)		175,176
t-BuNC	H	H	1.52 (80)	4.58 (90)		175
PPh_3	H	H	0.37 (88)	3.51 (112)		175,176
PEt_3	H	H	0.35 (80)	3.75 (94)		175,176
PMe_3	H	H	0.47 (83)	3.74 (95)		175,176
$P(C_2D_5)_3$	Me	Me	0.73 (74)			117
PMe_3	Me	Me	0.88 (77.4)		1.57 (5.0)	177
PEt_3	Me	Me	0.73 (75.1)		1.57 (4.4)	177
$P(i\text{-}Pr)_3$	Me	Me	0.86 (75.2)		1.49	121
PBu_3	Me	Me	0.85 (76.3)		1.56 (4.1)	177
PCy_3	Me	Me	0.98 (75.1)		1.58	121
PPh_3	Me	Me	0.87 (84.5)		1.40 (4.6)	177

Table 13. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of Unsubstituted Platina(IV)cyclobutanes

L	X	H^α ($^2J_{Pt-H}$)	H^β ($^3J_{Pt-H}$)	ref(s)
py	Cl	2.64 (83)	2.64	39,41
py	Br	2.80 (88)	2.44	181
4-Mepy	Cl	2.58 (83)	2.58	181
4-Mepy	Br	2.84 (88)	2.61	181
NH_3	Cl	2.07 (82)	2.40	181
NH_3	Br	2.44 (81)	2.61	181
1/2(en)	Cl	2.17 (78)	2.40	181
1/2(en)	Br	2.43 (83)	2.43	181

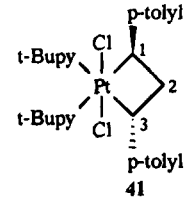
When a phosphorus ligand is coordinated to the platinum(II) in the unsubstituted examples, the α-proton chemical shift value ranges from 0.35 to 0.47 ppm. However, when the ligand is *t*-BuNC or bipy, the chemical shift value is 1.52 and 1.29 ppm, respectively. A similar influence is observed in the 2,2-dimethylplatina(II)cyclobutanes. These shift values are explained best by the increased donating ability of the phosphorus ligands which push electron density into the carbon ring system resulting in a more shielded proton environment.

The chlorine and bromine ligands coordinated to the platinum in the platina(IV)cyclobutanes in Table 13 also influence the chemical shift of the α protons. As illustrated, each platina(IV)cyclobutane bearing a bromine has an α-proton chemical shift consistently downfield of its chlorine analogue. The trend at the β position is inconsistent.

The effect of the ring substituents on the chemical shift value is a useful tool in determining the position of the substituents on the ring. This influence is illustrated for the platina(IV)cyclobutanes shown in Table 14. A drastic change occurs in the chemical shift value when a proton is bonded to a carbon bearing an alkyl or aryl substituent. For example, the α (no. 1 carbon) proton chemical shift of a platina(IV)cyclobutane with a phenyl substituent changes from 4.93 ppm when the phenyl is at the α position to 2.97 ppm when the phenyl group is at the β position.

The identification of platinacyclobutanes is aided also by the Pt–H coupling constants as shown in Tables 12–17. This information is particularly useful in determining the position of ring substituents. For example, when a methyl group is located α to the platinum the $^3J_{Pt-H}$ coupling to the methyl protons ranges from 22 to 45 Hz (Table 14). However, if the methyl is found β to platinum the $^4J_{Pt-H}$ coupling observed ranges from 4 to 8 Hz, making identification of isomers quite facile.

Table 16 illustrates the reported ^{1}H NMR data of trans-1,2-disubstituted platina(IV)cyclobutanes. A few trans-1,3-disubstituted platina(IV)cyclobutanes have been observed, as well. NMR data is reported only for the *trans*-1,3-di-*p*-tolylplatina(IV)cyclobutane **41**. In this example the α protons at positions 1 and

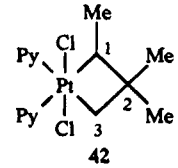


41

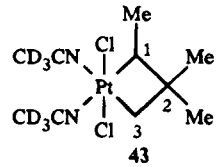
3 have a chemical shift value of 5.29 ppm and $^2J_{Pt-H}$ = 102 Hz which is slightly downfield of the 1,2-di-*p*-tolyl derivative and the ^3J coupling constant is slightly higher in the 1,3 system (entry 7, Table 16). The chemical shift of the protons β to platinum is reported as 3.29 ppm.[73]

The cis-disubstituted systems (Table 17), which are relatively new as stated earlier, exhibit ^{1}H chemical shifts in the same region as the 1,2 trans systems and the couplings are nearly equal as well. The norbornyl systems show more distinction but that is to be expected.

In Table 18, the ^{1}H NMR data of 1,2,3-trisubstituted platina(IV)cyclobutanes are reported. Data is also reported for two 1,2,2-trimethylplatina(IV)cyclobutanes (**42** and **43**). In complex **42** the α proton



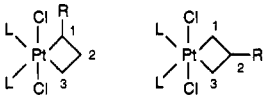
42



43

at the 1 position has a chemical shift value of 3.45 ppm. For the α protons at the 3 position, δ = 2.67

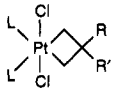
Table 14. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of Monosubstituted Platina(IV)cyclobutanes



L	R	H$^\alpha$ ($^2J_{Pt-H}$)	H$^\beta$ ($^3J_{Pt-H}$)	Me (J_{Pt-H})	ref(s)
py	1-Me			0.84 (22)	71,74
py	2-Me	2.67,3.02 (79,81)	3.08	1.30 (5)	74
py	2-Et	2.49,2.80 (78)			69
py	2-*i*-Pr	2.69 (90)			69
py	2-*n*-Bu	2.73 (80,82)			74
py	2-CH_2OH	2.47,2.61 (82.5,84.0)	3.06		77
py	2-CHMeOH	2.64,2.74 (84.8,85.0)	3.63		77
py	2-CMe_2OH	2.57,2.87 (80.8,84.6)	2.75		77
py	2-CH_2OMs	2.36,2.58 (81.5)			79
py	2-CHMeOPNB	2.2–3.2			79
py	2-CMe_2OPNB	2.54–3.02 (80,77)			79
py	1-Ph	4.93 (101)[a]			75
py	2-Ph	2.97 (82)	4.05		62,75
py	1-(*p*-MeC_6H_4)	4.93 (102)[a]	2.95		62,75
		2.95 (102)[b]			
py	2-(*p*-MeC_6H_4)	3.00 (80)	3.67		75
py	1-(*o*-MeC_6H_4)	4.90[a]			75
py	2-(*o*-MeC_6H_4)	2.97 (80)	3.6		75
py	2-(CH_2Ph)	2.97 (81)	3.21		62,74
py	2-(*n*-C_6H_{13})	2.42,2.75	3.75		62
py	2-(*o*-NO_2Ph)	2.98 (82)	4.56		62
py	1-(4-$MeOC_6H_4$)	5.03 (100)[a]			75
py	2-(4-$MeOC_6H_4$)	2.96 (83)			75
py	1-(4-$EtOC_6H_4$)	4.90 (100)[a]			75
py	2-(4-$EtOC_6H_4$)	2.90 (82)	3.65		75
2-Mepy	2-Ph	3.05 (80)	3.60		75
3-Mepy	1-Me			0.60 (22)	74
3-Mepy	2-Me	1.83,2.87 (76,78)	2.83	1.15	74
4-Mepy	1-Me	4.88 (100)[a]		0.68 (22)	74,75
4-Mepy	2-Me	2.06,2.69 (83,79)	2.72	1.00 (7)	74
4-Mepy	2-Ph	2.94 (81)	4.05		75
NH_3	2-Me			0.95	74
CD_3CN	1-Me			0.70 (36)	71,74,80
CD_3CN	2-Me	2.35,2.70		0.93 (4)	74,80
CD_3CN	2-Et	2.71			80
C_4D_8O	1-Me			0.46 (45)	74
C_4D_8O	2-Me	2.36,2.78 (109,108)	2.82	0.85 (8)	74
C_4D_8O	1-Ph	5.17 (113)[a]			75
C_4D_8O	2-Ph	3.10			75
C_4D_8O	1-(*p*-MeC_6H_4)	5.00 (120)[a]			75
C_4D_8O	2-(*p*-MeC_6H_4)	3.07 (80)	3.67		75
$^1/_2$(bipy)	2-CH_2OMs	2.37,2.61 (81.5,5.85)			79
$^1/_2$(tmed)	1-Me		2.6	0.62 (26.0)	80
$^1/_2$(tmed)	2-Me		2.6	0.89 (4.0)	80
$^1/_2$(tmed)	2-Et		2.25		80
$^1/_2$(tmed)	1-Ph	5.10 (101)[a]			75
$^1/_2$(tmed)	2-Ph	3.43 (84)	4.07		75
$^1/_2$(phen)	2-Me	2.44,2.72 (79,81)	2.74		74

[a] PtC*H*R. [b] PtCH_2.

Table 15. ^{1}H Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of 2,2-Disubstituted Platina(IV)cyclobutanes



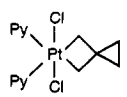
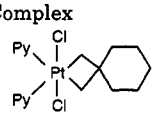
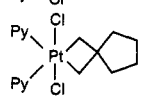
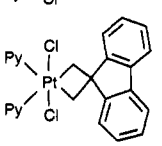
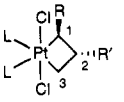
L	R	R′	H$^\alpha$ ($^2J_{Pt-H}$)	ref	L	R	R′	H$^\alpha$ ($^2J_{Pt-H}$)	ref
py	Me	Me	2.64 (85.5)	69	CD_3CN	Me	Me	2.54 (96.0)	80
py	Me	CH_2OMs	2.36 (85)	79	$^1/_2$(bipy)	Ph	CH_2OMs	2.96,3.20 (86.5,87)	79
py	Ph	CH_2OMs	2.95,3.23 (85,86)	79	$^1/_2$(tmed)	Me	Me	2.40 (84.0)	80
Complex									
			2.72 (82)	85				2.61 (84)	85
			2.71 (85)	85				3.17 (88)	182

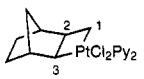
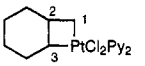
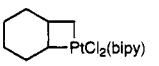
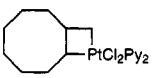
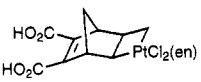
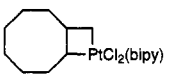
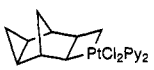
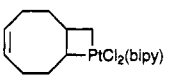
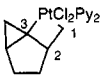
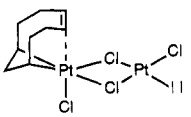
Table 16. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of Trans-1,2-Disubstituted Platina(IV)cyclobutanes



entry	L	R	R′	H^{α} ($^2J_{Pt-H}$)[a]	H^{β} ($^3J_{Pt-H}$)	H^{α} ($^2J_{Pt-H}$)[b]	Me(J_{Pt-H})	ref(s)
1	py	Me	Me	2.98 (88)	2.95	2.28,2.32 (79.5)	0.58 (22.8)[c] 0.94 (7.2)[d]	73
2	py	Ph	Ph	5.12 (98)	4.75	3.2 (77,84.5)		62,73
3	py	Ph	Me	4.56 (99)		2.67 (80)	0.96	71,73
4	py	Me	Ph				0.61 (24)	71,73
5	2-Mepy	Me	Me				0.40 (32)[c] 0.83[d]	73
6	*t*-Bupy	Ph	Ph	5.13 (98)	4.78	3.26 (80.5)		73
7	*t*-Bupy	*p*-tol	*p*-tol	5.11 (97)	4.76	3.27 (80.5)		73
8	PhCN	Me	Me				0.60 (38)[c] 0.78[d]	73
9	CD_3CN	Me	Me				0.60 (37)[c] 0.73 (14)[d]	73
10	$^1/_2$(phen)	Me	Me				1.15 (22)[c] 1.05[d]	73

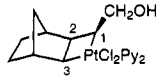
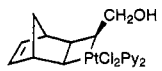
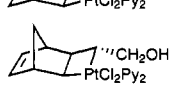
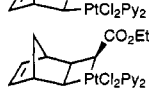
[a] H^{α} is bonded to carbon labeled 1. [b] $H^{\alpha'}$ is bonded to carbon labeled 3. [c] 1-Me. [d] 2-Me.

Table 17. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of Cis-Disubstituted Platina(IV)cyclobutanes

complex	H^{α} ($^2J_{Pt-H}$)[a]	H^{β} ($^3J_{Pt-H}$)	$H^{\alpha'}$ ($^2J_{Pt-H}$)[b]	ref	complex	H^{α} ($^2J_{Pt-H}$)[a]	H^{β} ($^3J_{Pt-H}$)	$H^{\alpha'}$ ($^2J_{Pt-H}$)[b]	ref
	2.47,2.51	2.77	2.74	76		2.8,3.0	3.0	3.7 (93)	89
	2.72,2.76	2.48	2.34	76		2.4,2.7 (80,85)	3.1	3.3 (92)	89
	2.8	2.7	2.5	97		2.5,2.66	2.7	3.6 (96)	184
	2.35	2.40	2.04	97		2.4,2.6 (91)	2.9	3.5 (98)	184
	2.55–2.65	2.93	2.79	183		1.8–2.5, 2.6 (91)	3.15	3.6 (95)	184
	2.87,3.10 (80,76)	3.05		95		1.28 (108)	2.22–2.6, 2.96 (92)		184

[a] H^{α} is bonded to carbon labeled 1. [b] $H^{\alpha'}$ is bonded to carbon labeled 3.

Table 18. ^{1}H NMR Chemical Shift (ppm) Data of 1,2,3-Trisubstituted Platina(IV)cyclobutanes

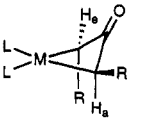
complex	H^{α} [a]	H^{β}	$H^{\alpha'}$ [b]	ref
	3.55	2.89	2.70	76
	3.90	2.45	2.52	76
	4.12	2.85	3.06	76
	5.16	2.80	2.85	76

[a] H^{α} is bonded to carbon labeled 1. [b] $H^{\alpha'}$ is bonded to carbon labeled 3.

ppm.[69] For complex **43**, the α proton at position 1 has a chemical shift of 3.27 ppm, while the chemical shift value of the α protons at position 3 is reported as 2.43 ppm[80] which is a clear upfield shift due to ligand change.

The reported ^{1}H NMR data for low-valent (save entries 2 and 3 in Table 22) metallacyclobutanones is exhibited in Tables 19–22. Table 19 reports the ^{1}H NMR data of the α protons of pallada(II)- and platina(II)cyclobutanones. The puckered structure of these metallacyclic complexes causes the ring substituents (**R**) at the two α positions to adopt a pseudoequatorial and a pseudoaxial configuration. This in turn forces one α proton into an axial position while the other becomes equatorial. If the ^{1}H NMR data are collected at low temperatures, it is possible to identify the individual chemical shifts. However, if the data is recorded at room temperature the peaks formed from these two nonequivalent protons become equivalent and indistinguishable due to rapid inversion of the ring. In the resolved spectral data (Table

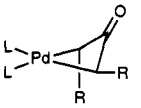
Table 19. Low-Temperature[a] ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant (Hz) Data of Pallada(II)- and Platina(II)cyclobutanones



M	L	R	H_a ($^2J_{Pt-H}$)	H_e ($^2J_{PtH}$)	ref	M	L	R	H_a ($^2J_{Pt-H}$)	H_e ($^2J_{PtH}$)	ref
Pd	PPh_3	CO_2Me	4.54	3.71	156	Pt	PPh_3	H	2.25 (48.4)	2.01,2.25	162
Pd	PEt_3	CO_2Me	4.22	3.67	157	Pt	PPh_3	COMe	4.53 (49.9)	3.80 (29.0)	159
Pd	PPh_2Me	CO_2Me	4.36	3.78	157	Pt	PPh_3	CO_2Me	4.05 (74)	3.24 (23.8)	159
Pd	$PPhMe_2$	CO_2Me	4.45	3.96	157	Pt	$AsPh_3$	CO_2Me	4.02 (83.2)	3.67 (36.0)	159
Pd	$^1/_2$(bipy)	CO_2Me	4.49	3.67	157	Pt	$AsPh_3$	COMe	4.52 (81.2)	4.09 (51.2)	159
Pd	$AsPh_3$	CO_2Me	4.48	4.00	157						

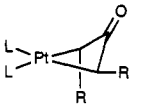
[a] −50° to −100 °C.

Table 20. ^{1}H NMR Chemical Shift Data (ppm) of Pallada(II)cyclobutanones



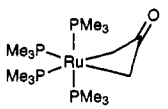
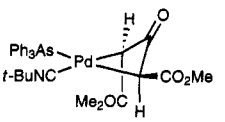
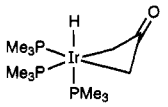
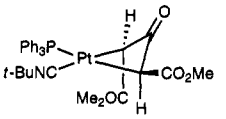
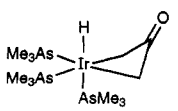
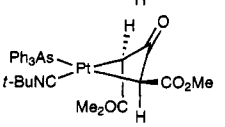
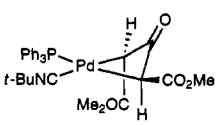
L	R	H^α	ref	L	R	H^α	ref
PEt_3	CO_2Me	3.98	157	$^1/_2$(bipy)	CO_2Me	4.07	157
PEt_3	Ph	3.87	163	$^1/_2$(bipy)	CO_2Et	3.82	157
PPh_3	CO_2Me	4.11	157	$^1/_2$(bipy)	CO_2-*n*-Pr	3.86	157
PPh_3	CO_2Et	4.09	157	$^1/_2$(dppe)	Ph	3.99	163
PPh_3	Ph	4.15	163	$AsPh_3$	CO_2Me	4.22	157
PPh_2Me	CO_2Me	4.00	157	$AsPh_3$	CO_2Et	4.33	157
$PPhMe_2$	CO_2Me	4.26	157				

Table 21. ^{1}H NMR Chemical Shift (ppm) and Pt–H Coupling Constant Data (Hz) of Platina(II)cyclobutanones



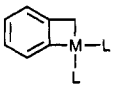
L	R	δH^α ($^2J_{Pt-H}$)	ref	L	R	δH^α ($^2J_{Pt-H}$)	ref
PPh_3	CO_2Me	3.73 (54.17)	154	$^1/_2$(dppe)	CO_2Me	4.37 (53.6)	154
PPh_3	CO_2Et	3.90 (52.2)	154	$AsPh_3$	CO_2Me	4.16 (71.64)	154
PPh_3	CO_2-*n*-Pr	3.92 (52.8)	154	$AsPh_3$	CO_2Et	4.09 (69.9)	154
PPh_3	COMe	4.20 (47.8)	160	$AsPh_3$	CO_2-*n*-Pr	4.12 (69.6)	154
PPh_3	Ph	4.01 (84.2)	163	$AsPh_3$	COMe	4.31 (65.6)	160
PPh_2Me	CO_2Me	3.96 (55.5)	154	$AsPh_3$	Ph	4.14 (100.29)	163
$PPhMe_2$	CO_2Me	4.07 (55.2)	154	$^1/_2$(cod)	Ph	3.99 (104.4)	163

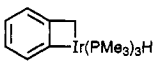
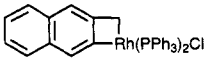
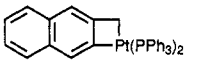
Table 22. ^{1}H NMR Chemical Shift (ppm) Data of Other Metallacyclobutanones

entry	complex	H^α	ref	entry	complex	H^α	ref
1		1.54	185	5		3.69,4.64	158
2		2.20,3.10	131	6		3.69,[a,e]4.46[b,f]	158
3		2.49,3.10	131	7		3.90,[c,g]4.44[d,h]	158
4		4.02,[a]4.62[b]	158				

[a] Equatorial proton trans to *t*-BuNC. [b] Axial proton trans to PPh_3. [c] Equatorial proton trans to $AsPh_3$. [d] Axial proton trans to *t*-BuNC. [e] $^2J_{Pt-H}$ = 46.0. [f] $^2J_{Pt-H}$ = 71.8. [g] $^2J_{Pt-H}$ = 49.3.

Table 23. ^{1}H NMR Chemical Shift (ppm) Data of Rhoda(III)-, Irida(III)-, Nickela(II)-, and Platina(II)cyclobutabenzenes

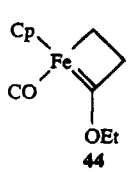


entry	M	L	H^a	ref
1	Ni	PEt_3	0.41	112
2	Ni	PBu^n_3	0.38	112
3	Ni	PPh_3	0.55	112
4	Ni	$^1/_2$(tmed)	−0.26	112
5	Pt	PMe_3	1.13^a	178
6	Pt	PMe_3	2.06^b	178
7	Pt	PEt_3	1.57^c	178
8	Pt	PPh_3	1.61	178
		Complex		
9			2.16	131
10			2.16^d	115
11			1.23^e	115

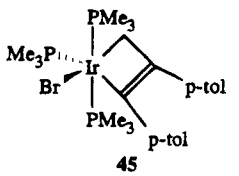
^{a} $^2J_{Pt-H}$ = 67.9 in dioxane-d_8. ^{b} In benzene-d_6. ^{c} $^2J_{Pt-H}$ = 78.3. ^{d} $^2J_{Rh-H}$ = 3.9. ^{e} $^2J_{Pt-H}$ = 79.

19), the axial proton is consistently downfield of the equatorial proton and the ^2J coupling constant is also considerably larger. Furthermore, the α protons in the platinum complexes are always upfield of those in the palladium complexes where equivalent structures are available.

Only two metallacyclobutene complexes have reported ^{1}H NMR data. The report for the ferra(II)-cyclobutene **44** gives a multiplet at 2.5−1.7 ppm assignable to the CH_2 groups of the metallacyclic ring.[170] The report for the irida(III)cyclobutene **45** is that the chemical shift of the α protons is 1.16 ppm.[168]



44



45

The reported ^{1}H NMR data of metallacyclobutabenzenes is displayed in Table 23. The data for the Pt(II) and Ni(II) examples are indicative of the effect of the metal on proton chemical shifts. Where comparable, nickel shows a considerable shift to higher field for the alpha protons. Unfortunately, either the differences in oxidation states or ligands prevents valid comparisons between iridium, rhodium, and platinum (entries 9, 10, and 11).

B. ^{13}C NMR Spectroscopy

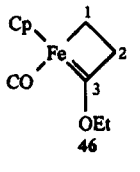
Tables 24−33 display the reported ^{13}C NMR chemical shift (ppm) and metal−carbon coupling constant (Hz) data (where applicable) for metallacyclobutane derivatives. Again, the data repeatedly confirms the utility of this form of spectroscopy in the characterization of metallacyclic complexes.

As was apparent in the reported ^{1}H NMR data, the amount of ^{13}C NMR data is largest for platina(IV)-cyclobutanes. This information is particularly valuable for distinguishing between isomers of platina(IV)cyclobutanes. Table 26 depicts platina(IV)-cyclobutanes that are substituted at either the 1 or 2 position. It is apparent that three unique ring carbon peaks are present when the ring has unsymmetrical substitution and two carbon ring resonances when the substituent(s) yield a symmetrical cyclobutane ring. Endless comparisons can be made here but the authors will leave this exercise to the reader.

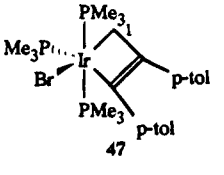
The Pt−C coupling constants observed in the spectra of platina(II)- and -(IV)cyclobutanes provide additional characterization of these complexes. These coupling constant values are large and readily observed in routine spectra. Tables 28 and 29 illustrate the characteristic Pt−C coupling constant values for a variety of norbornyl systems containing a platina(IV)cyclobutane moiety. On average, the $^1J_{Pt-C}$ constant is 350 (Hz) and the $^2J_{Pt-C}$ constant is near 100 Hz. A $^3J_{Pt-C}$ constant to the distal carbon of the norbornyl ring is of the order of 40 Hz.

Pallada(II)- and platina(II)cyclobutanones also exhibit characteristic ^{13}C NMR data as demonstrated in Table 30. The chemical shift values range from 48.8 to 67.06 ppm for C^1 and from 171.21 to 183.8 ppm for C^2. The ^{13}C NMR data of other metallacyclobutanones is shown in Table 31. Notice that the pallada(II)- and platina(II)cyclobutanes found in Table 31 have two different ligands coordinated to the metal, therefore making the α ring carbons nonequivalent and resulting in three unique carbon resonances. The α carbons of the platinum complex resonate upfield of the palladium analogue but the β-carbon resonances are reversed. Further, the $^2J_{Pt-C}$ constant is larger by nearly double in these cases relative to the cyclobutane system. This can be viewed as evidence for transannular participation or enhanced ^2J coupling due to increases in s character in the bonds.

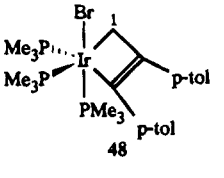
^{13}C NMR chemical shift data for metallacyclobutenes of iron(II) and iridium(III) have been reported as shown below. Complex **46** exhibits resonances at 61.6, 56.8, and 335 ppm for carbons labeled 1, 2, and 3, respectively. Compounds **47** and **48** exhibit resonances for their respective C^1 labeled carbons at −17.96 and −8.76 ppm.



46



47



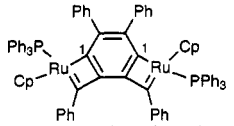
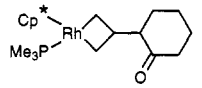
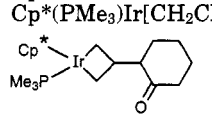
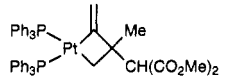
48

A number of nickel(II)cyclobutabenzenes have been characterized by ^{13}C NMR spectroscopy. Table 32 exhibits these data while Table 33 displays the ^{13}C NMR data for other metallacyclobutabenzenes.

C. Summary of NMR Spectroscopy

There is a great deal of data presented in this section on NMR spectroscopy. A few comparisons have been made but many more are available. Our goal here is to collect and make the data available for comparison to new complexes and for those who wish to use the results for bonding arguments. For

Table 24. ^{13}C NMR Chemical Shift (ppm) Data of Ruthena(II)-, Osmia(II)-, Rhoda(III)-, Irida(III)-, and Platina(II)cyclobutanes

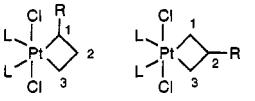
complex	C^1	C^2	C^3	ref
	138.3			167
$(CO)_4Os[CH_2CH_2CH_2]$	−38.01	39.04		174
$Cp^*(PMe_3)Rh[CH_2CH_2CH_2]$	−22.85	31.33		172
$Cp^*(PMe_3)Rh[CH_2CMe_2CH_2]$	−23.1	43.21		172
$Cp^*(PPh_3)Rh[CH_2CMe_2CH_2]$	−1.85	38.50		125
$Cp(P(i\text{-}Pr)_3)Rh[CHMeCH_2CH_2]$	−30.9[a]	43.9[a]	−10.6[a]	144
	−11[b]	43.4	−11.5[b]	137
$Cp^*(C_2H_4)Ir[CH_2CH_2CH_2]$	−31.7	31.3		142
$(PMe_3)_3HIr[CH_2CMe_2CH_2]$	−17.87	45.75		131
$(AsMe_3)_3HIr[CH_2CMe_2CH_2]$	−20.96	47.28		131
$Cp^*(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[c]	−23.0		−24.1	142
$Cp^*(C_2H_4)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[d]	−19.3		−20.7	142
$Cp^*(PMe_3)Ir[CH_2CH(CHMeC(O)Ph)CH_2]$[d]	−28.6		−29.2	137
	−29.7	46.8	−30.3	137
$(PPh_3)_2Pt[C(CN)_2CH_2C(CN)_2]$	−23.1	48.4		102[b]
$(PMePh_2)_2Pt[C(CN)_2CH_2C(CN)_2]$	−26.8[f]	48.3		102[b]
$(AsPh_3)_2Pt[C(CN)_2CH_2C(CN)_2]$	−30.7[g]	49.5		102[b]
$(PPh_3)_2Pt[CH_2CH(CMe_2COOMe)CH_2]$	−7.3[h]	50.8[h]		139
$(P(C_6H_{11})_3)_2Pt[CH_2CH(CMe_2COOMe)CH_2]$	−10.2[i]	51.2[i]		139
$(dppe)Pt[CH_2CH(CHMeCOOMe)CH_2]$	−8.7[j]	47.4[j]	−7.1	139
$(PPh_3)_2Pt[CH_2C(Me)(CMe_2COOMe)CH_2]$	1.5[k]	50.3[k]		139
$(PPh_3)_2Pt[CH(Me)CH(CMe_2COOMe)CH_2]$[l]	−2.8[l]	60.0[l]	−10.3[l]	139
$(PPh_3)_2Pt[CH(Me)CH(CMe_2COOMe)CH_2]$[m]	9.9	53.7[m]	−6.8	139
	141.2[n]	58.5[n]	9.2[n]	138

[a] Me is bonded to C^1; $^1J_{Rh-Cl} = 19.3$; $^2J_{Rh-C} = 6.6$; $^1J_{rh-C3} = 19.5$. [b] $^1J_{Rh-C} = 10.2$. [c] Ring substituent is syn to Cp*. [d] Ring substituent is anti to Cp*. [e] $^1J_{Pt-C} = 450$; $^2J_{Pt-C} = 160$. [f] $^1J_{Pt-C} = 450$; $^2J_{Pt-C} = 155$. [g] $^1J_{Pt-C} = 365$; $^2J_{Pt-C} = 180$. [h] $^1J_{Pt-C} = 413$; $^2J_{Pt-C} = 128$. [i] $^1J_{Pt-C} = 430$; $^2J_{Pt-C} = 128$. [j] $^1J_{Pt-C} = 398$; $^2J_{Pt-C} = 139$. [k] $^1J_{Pt-C} = 415$; $^2J_{Pt-C} = 116$. [l] Ring substituents trans, Me is bonded to C^1; $^1J_{Pt-Cl} = 459$; $^2J_{Pt-C} = 128$; $^1J_{Pt-C3} = 420$. [m] Ring substituents cis, Me is bonded to C^1; $^2J_{Pt-C} = 130$. [n] Methylene is bonded to C^1; $^2J_{Pt-C} = 130$; $^1J_{Pt-C3} = 437.5$.

Table 25. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant (Hz) Data of Unsubstituted Platina(IV)Cyclobutanes

L	X	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	ref	L	X	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	ref	L	X	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	ref
py	Cl	−15.2 (335)	30 (105)	181	4-Mepy	Cl	3.77 (338)	29.9 (105)	181	½(en)	Cl	−18.9 (332)	29.6 (108)	181
py	Br	−17.9 (325)	30.4 (110)	181	4-Mepy	Br	−18.5 (323)	30.5 (103)	181	½(en)	Br	−21.4 (317)	30.4 (105)	181

Table 26. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant (Hz) Data of Monosubstituted Platina(IV)cyclobutanes



L	R	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
py	1-Me	5.65	45.2	−8.0	71,74
py	2-Me	1.0 (344)	42.6 (98)		71,74
py	1-Bu	11.8		−7.9	74
py	2-Bu	−5.2 (344)	43.4 (95)		71,74
py	2-CH_2OH	−11.3 (350.1)	45.6 (99.1)		77
py	2-CHMeOH	−11.1 (351.0)	51.1 (96.2)	−10.5 (349.2)	77
py	2-CMe_2OH	−10.5 (352.3)	54.1 (94.1)		77
py	2-CH_2CO_2Me	−7.64 (349.2)	39.13 (101.5)		76
py	1-COMe	3.2 (351)	30.5 (107)	−10.4 (328)	98

Table 26 (Continued)

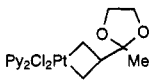
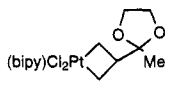
L	R	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
py	2-COMe	−12.5 (364)	55.9 (103)		98
py	2-CH_2OMs	−13.7 (356)	42.1 (104)		78,79
py	2-CHMeOPNB	−11.6 (358)	48.5 (101)	−10.6 (355)	79
py	2-CMe_2OPNB	−9.8 (361)	54.8 (97.5)		79
py	1-Ph	5.6 (326)	35.1 (112)	−11.3 (354)	68,75
py	2-Ph	−4.9 (369)	48.1 (100.5)		68,75
py	1-(*p*-MeC_6H_4)	5.80 (323)	35.3 (112)	−11.5 (366)	75
py	2-(*p*-MeC_6H_4)	−4.30 (370)	47.8 (99)		75
py	1-(4-$EtOC_6H_4$)	5.75 (320)	35.5 (115)	−11.9 (360)	75
py	2-(4-$EtOC_6H_4$)	−4.30 (360)	46.97 (105)		75
py	2-NH_2	−11.6 (466)	60.4 (107.7)		81
4-Mepy	1-Ph	4.29 (330)	37.6 (114)	−11.8 (372)	75
4-Mepy	2-Ph	−5.13 (358)	48.11 (99)		75
1/2(bipy)	2-CH_2OMe	−12.4 (357)	55 (99)		98
1/2(tmed)	1-Ph	7.15 (329)	38.0 (112)	−7.6 (359)	75
1/2(tmed)	2-Ph	−3.10 (370)			75
C_4D_8O	1-Me	5.5	40.6	−12.8	74
C_4D_8O	2-Me	−5.1 (398)	37.6 (109)		74
C_4D_8O	1-(*p*-MeC_6H_4)	6.07 (397)	34.9 (127)	−13.9 (429)	75
C_4D_8O	2-(*p*-MeC_6H_4)	−7.57 (418)	47.0 (111)		75
		Complex			
		−10.6 (349)	50.5 (95)		98
		−12.5 (358)	49.7 (98)		98

Table 27. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant (Hz) Data for Trans-1,2-Disubstituted, Trans-1,3-Disubstituted, and 2,2-Disubstituted Platina(IV)cyclobutanes

L	R	R′	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
py	1-Me	2-Me	10.9 (336)	46.4 (98)	−2.6 (347)	73
py	1-Me	2-Ph	10.6 (360)	57.5 (100)	−2.9 (370)	71,73
py	1-Ph	2-Me	16.9 (333)	41.2 (103)	−0.2 (263.5)	71,73
t-Bupy	1-Ph	2-Ph	15.1 (343)	50.6 (105)	−1.8 (377)	71,73
t-Bupy	1-(*p*-tolyl)	2-(*p*-tolyl)	15.7 (341)	50.5 (105)	−1.6 (383)	71,73
t-Bupy	1-Ph	3-Ph	6.05 (340)	41.2 (130)		71,73
t-Bupy	1-(*p*-tolyl)	3-(*p*-tolyl)	6.3 (338)	41.6 (125)		71,73
py	2-Me	2-CH_2OH	−3.0 (355.7)	48.7 (92.2)		77
py	2-Me	2-CH_2OMs	−4.9 (361)	46.9 (95)		79
py	2-Ph	2-CH_2OMs	−6.7 (367)	56.0 (90)		79
			−4.65 (376)	60.9 (95)		182

Table 28. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant (Hz) Data for Cis-Disubstituted Platina(IV)cyclobutanes

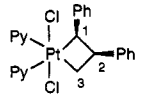
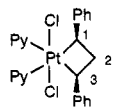
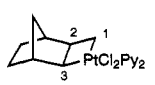
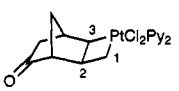
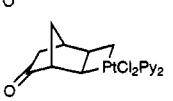
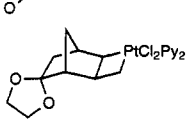
complex	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
	14.9 (353.4)	51.7 (109.93)	−8.6 (364.4)	94
	10.5 (347.2)	39.5 (116.6)		94
	−12.1 (352)	55.6 (95)	12.4 (391)	183
	−13.56 (362)	47.16 (100)	5.20 (412)	93
	−10.65 (351.5)	52.71 (98.3)	−2.21 (429.3)	93
	−12.9 (355.8)	54.0 (97.6)	9.5 (399.3)	93

Table 28 (Continued)

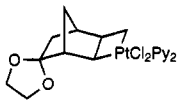
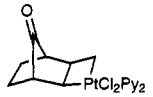
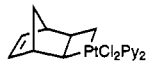
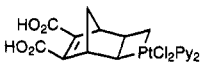
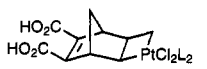
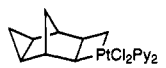
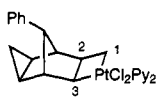
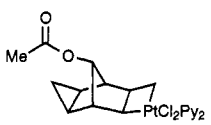
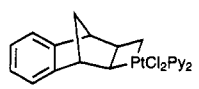
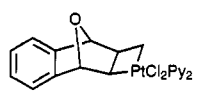
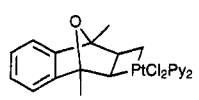
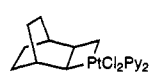
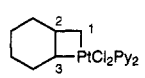
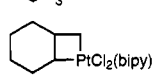
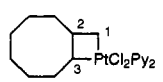
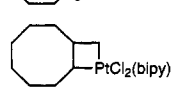
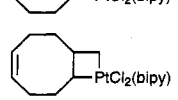
complex	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
	−11.2 (352.3)	47.8 (98.4)	2.7 (408.2)	93
	−12.1 (352)	53.9 (95)	9.2 (391)	81
	−12.3 (351)	51.1 (99)	2.7 (405)	81
	−2.2 (371)	51.4 (83)	10.7 (403)	87
	−3.7 (366)	51.25 (90)	5.8 (422)	76
	−5.54 (345)	51.6 (87.4)	7.23 (383)	76
	−3.6 (373.3)	52.3 (85.0)	5.9 (423.2)	97
L = (4-pyridyl)carbinol				
	−3.8 (387)	51.0	5.85 (430)	76
	−2.5 (374.6)	52.1 (84.2)	10.7 (406.2)	92
	−12.1 (352)	55.6 (95)	12.4 (391)	79,88
	−8.6 (363.0)	57.3 (95.3)	13.7 (398.6)	92
	−8.6 (359)	54.9 (95)	8.1 (406)	81
	−5.7 (365)	56.6 (97)	10.1 (408)	76
	−6.39 (364)	52.36 (96)	5.37 (440)	76
	−8.63 (361)	58.0 (94)	13.7 (444)	81
	−12.9 (352)	49.3 (94)	11.9 (387)	92
	−8.6 (354)	44.6 (98)	5.8 (369)	88
	−7.7 (342)	42.8 (92)	5.2 (366)	89
	−7.2 (351)	48.6 (85)	14.2 (348)	88
	−6.7 (364)	47.4 (85)	13.3 (342)	184
	−6.1 (361)	47.8 (82)	12.5 (345)	88

Table 28 (Continued)

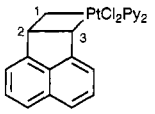
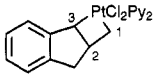
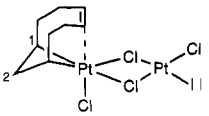
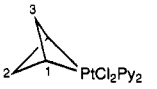
complex	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref(s)
	−4.99 (366.2)	55.06 (106.9)	5.28 (363.5)	94
	−4.71 (348.7)	48.23 (102.4)	10.71 (354.9)	94
	29.6 (338)	36.8 (100)		66
	19.7 (621)	45.6		90

Table 29. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant (Hz) Data for 1,2,3-Trisubstituted Platina(IV)Cyclobutanes

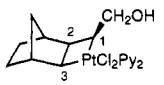
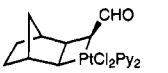
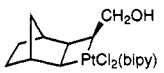
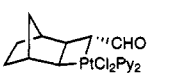
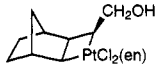
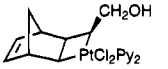
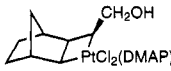
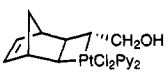
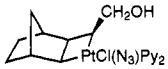
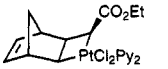
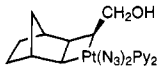
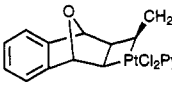
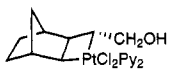
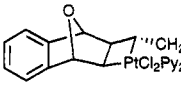
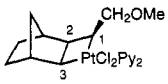
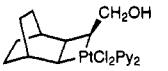
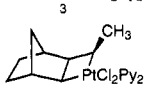
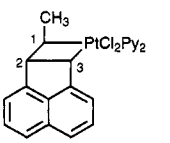
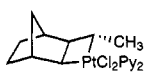
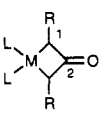
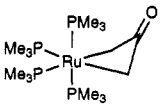
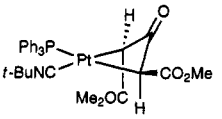
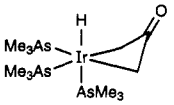
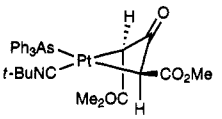
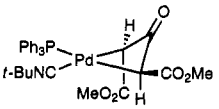
complex	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref	complex	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	C^3 ($^1J_{Pt-C}$)	ref
	6.36 (370)	56.7 (98)	13.0 (394)	96		4.35 (352)	55.6 (106)	15.2 (380)	92
	1.83 (363.0)	56.5 (95.7)	9.8 (396.1)	97		4.8 (348)	53.9 (103)	15.7 (377)	92
	1.9 (366.2)	56.3 (99.2)	7.1 (391.3)	97		15.8 (394)	52.72 (86.1)	11.14 (405)	76
	4.46 (366)	56.5 (98)	10.6 (394)	81		14.6 (392)	54.24 (81.3)	12.45 (404)	76
	2.4 (392)	55.7 (101)	11.0 (421)	81		3.0 (406)	53.2 (87)	3.3 (394)	76
	1.7 (424)	53.5 (109)	10.6 (451)	81		12.3 (400)	54.1 (104)	6.1 (450)	76
	4.05 (370)	59 (98)	14.4 (398)	96		11.2 (396)	55.8 (104)	7.9 (458)	76
	0.5 (373)	57.5 (97)	13.7 (394)	81		11.0 (371)	52.1 (96)	11.3 (395)	81
	1.33 (351)	59.16 (97)	12.07 (401)	92		6.38 (385.8)	64.02 (105.7)	10.73 (372.7)	94
	1.40 (355)	64.49 (97)	12.9 (394)	92					

Table 30. ^{13}C NMR Chemical Shift (ppm) and Pt−C Coupling Constant Data for Pallada(II)- and Platina(II)cyclobutanones



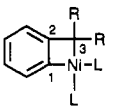
M	L	R	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	ref	M	L	R	C^1 ($^1J_{Pt-C}$)	C^2 ($^2J_{Pt-C}$)	ref
Pd	PPh_3	CO_2Me	61.82	174.42	157	Pt	PPh_2Me	CO_2Me	54.84 (245)	179.73 (170)	154
Pd	PPh_2Me	CO_2Me	59.26	171.21	157	Pt	$PPhMe_2$	CO_2Me	53.24 (229.3)	179.00 (171)	154
Pd	$PPhMe_2$	CO_2Me	57.34	175.52	157	Pt	1/2(dppe)	CO_2Me	54.89 (231.0)	178.47 (161)	154
Pt	PPh_3	CO_2Me	56.43 (273.9)	178.30 (175.5)	154	Pt	$AsPh_3$	CO_2Me	51.21 (313.9)	179.26 (195)	154
Pt	PPh_3	COMe	67.06 (246.9)	176.17 (173.7)	160	Pt	$AsPh_3$	COMe	63.28 (298.1)	179.08 (196.3)	160
Pt	PPh_3	Ph	67.07 (242.4)	173.2 (155)	163	Pt	$AsPh_3$	Ph	61.52 (308.4)	174.39	163
Pt	PPh_3	H	49.6 (251.5)	183.8	162	Pt	1/2(cod)	Ph	63.28 (351.7)	178.6	163

Table 31. ^{13}C NMR Chemical Shift (ppm) Data of Other Metallacyclobutanones

complex	C^1	C^2	C^3	ref	complex	C^1	C^2	C^3	ref
	29.13	184.0		185		51.3[a,c]	179.6[c]	51.0[b,c]	158
	12.32	185.06		131		48.8[a,d]	179.8[d]	48.2[b,d]	158
	56.9[a]	175.2	55.7[b]	158					

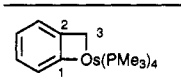
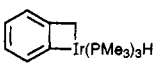
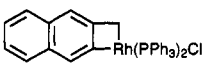
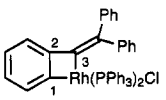
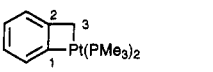
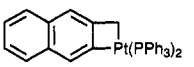
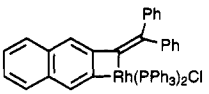
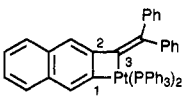
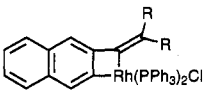
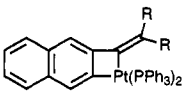
[a] C^1 is trans to *t*-BuNC. [b] C^3 is cis to *t*-BuNC. [c] $^1J_{Pt-C1} = 293$; $^2J_{Pt-C} = 177$; $^1J_{Pt-C3} = 216.5$. [d] $^1J_{Pt-C1} = 288.8$; $^2J_{Pt-C} = 189.4$; $^1J_{Pt-C3} = 267.7$.

Table 32. ^{13}C NMR Chemical Shift (ppm) Data for Nickela(II)cyclobutabenzenes



L	R	C^1	C^2	C^3	ref	L	R	C^1	C^2	C^3	ref
PEt_3	H	134.7	160.5	−6.3	112	$^1/_2$(dcpe)	$SiMe_3$	127.5	161.6	−1.68	114
PBu_3	H	134.2	160.7	−7.1	112	$^1/_2$(dppe)	$SiMe_3$	125.3	162.0	0.93	114
PPh_3	H	134.5	158.0	0.5	112	$^1/_2$(TEED)	$SiMe_3$	113.8	158.9	−17.3	114
$^1/_2$(tmed)	H	128.6	159.1	−17.1	112	$^1/_2$(PMDTA)	$SiMe_3$	113.8	159.5	−16.5	114
$^1/_2$(tmed)	$SiMe_3$	115.5	159.8	−17.1	114	$^1/_2$(bipy)	$SiMe_3$	119.0	159.6	−8.67	114
PMe_3	$SiMe_3$	127.3	162.7	−3.29	114						

Table 33. ^{13}C NMR Chemical Shift (ppm) Data of Other Metallacyclobutabenzenes

complex	C^1	C^2	C^3	ref	complex	C^1	C^2	C^3	ref
		168.3	−16.5	130			153.59		
			−7.15	131			150.0[d]	−2.9[d]	115
	119.9, 112.3[a]	156.70[a]	117.7[a]	116				−9.9[e]	178
	124.08							−3.21	115
		154.83[b]	117.0[b]	116		147.26[f]	165.64[f]	113.84[f]	116
		141.72, 145.10[c]	166.67[c]	116		139.68	166.06		116
R = *m*-$CF_3C_6H_4$					R = *p*-$MeOC_6H_4$				

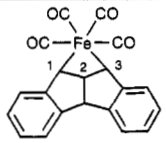
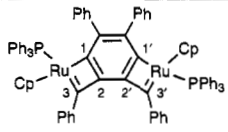
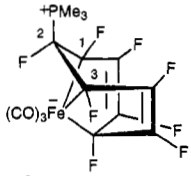
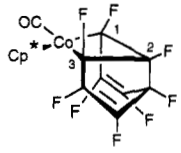
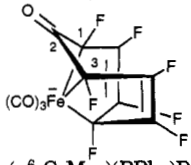
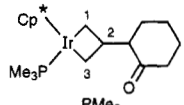
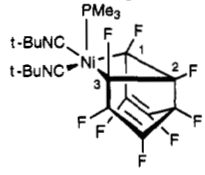
[a] Assignments for C^1 and C^3 may be interchanged; $^1J_{Rh-C1} = 21.0$; $^2J_{Rh-C} = 3.9$; $^1J_{Rh-C3} = 28.2$. [b] $^2J_{Rh-C} = 3.8$; $^1J_{Rh-C3} = 28.7$. [c] $^2J_{Rh-C} = 3.3$; $^1J_{Rh-C3} = 28.6$. [d] $^2J_{Rh-C} = 6.3$; $^1J_{Rh-C3} = 21$. [e] $^1J_{Pt-C3} = 395$. [f] $^1J_{Pt-C1} = 86$; $^2J_{Pt-C2} = 65$; $^1J_{Pt-C3} = 81$.

the structure determination chemist, it appears that the ^{13}C data are the most definitive as the sensitivity of ^{13}C chemical shifts to structural variation is the greatest. It is believed that coupling constant data will be helpful, in the future, to predict chemical reactivity.

D. X-ray Crystallographic Analysis

X-ray structure determinations have been performed on relatively few metallacyclobutane derivatives. Tables 34−43 display the bond length and bond angle data for the metallacyclobutane moiety of the reported structures. The written structures are all in a M[$C_1C_2C_3$] format, while the drawn structures are labeled appropriately. These data consistently support a metallacyclobutane structure as opposed to an edge-bound cyclopropane. The reported C_1-C_3 distance, ranging from 2.37 to 2.60 Å, most convincingly eliminates the notion that the cyclopropane ring remains intact and is bound edge-

Table 34. Bond Length Data (Å) for Ferra(II)-, Ruthena(II), Cobalta(II)-, Rhoda(III)-, Irida(III)-, and Nickela(II)cyclobutanes

entry	complex	M–C$_1$	M–C$_2$	M–C$_3$	C$_1$–C$_2$	C$_2$–C$_3$	entry	complex	M–C$_1$	M–C$_2$	M–C$_3$	C$_1$–C$_2$	C$_2$–C$_3$
1		2.141	2.691	2.137	1.524	1.527[a]	6		2.051		1.997	1.41	1.432
									2.062[b]		1.982	1.411	1.44
2		2.013		2.006	1.536	1.519	7		1.993		1.986	1.525	1.526
3		2.039		2.036	1.486	1.492	8	(Cp*)(PMe$_3$)Rh-[CH$_2$CH$_2$CH$_2$]	2.085		2.085	1.512	1.527
4	(η^6-C$_6$Me$_6$)(PPh$_3$)Ru-[CH$_2$CMe$_2$CH$_2$]	2.133		2.144	1.537		9		2.126		2.114	1.539	1.531
5	(η^5-C$_6$Me$_6$)(PPh$_2$Me)-Ru[CH$_2$CMe$_2$CH$_2$]	2.156		2.133	1.546		10		1.995			1.527	

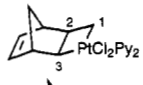
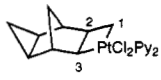
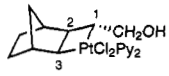
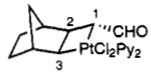
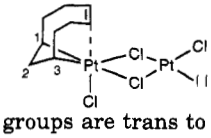
[a] C$_1$–C$_3$ = 2.421. [b] This row designates the carbons labeled prime.

Table 35. Bond Angle Data (deg) for Ferra(II)-, Ruthena(II)-, Cobalta(II)-, Rhoda(III)-, Irida(III)- and Nickela(II)cyclobutanes

entry	C$_1$–M–C$_3$	C$_1$–C$_2$–C$_3$	M–C$_1$–C$_2$	M–C$_3$–C$_2$	dihedral[a]	ref(s)	entry	C$_1$–M–C$_3$	C$_1$–C$_2$–C$_3$	M–C$_1$–C$_2$	M–C$_3$–C$_2$	dihedral[a]	ref(s)
1	68.9	105.0	93.0	93.0	0.0	186	6	64.8[b]					167
2						153	7	72.87				4.1	151
3						153	8	67.61	99.55	96.24	96.59	0.0	135,172
4	65.8		96.6		0.052	127	9	66.3	98.1	94.2	94.9		137
5	66.8		95.4		0.053	127	10		72.98	99.2		5.5	150

[a] The angle formed between the planes of C$_1$–M–C$_3$ and C$_1$–C$_2$–C$_3$. [b] Angle of atoms labeled prime is also 64.8°.

Table 36. Bond Length (Å) Data for Platina(II)- and Platina(IV)cyclobutanes

entry	complex	M–C$_1$	M–C$_2$	M–C$_3$	C$_1$–C$_2$	C$_2$–C$_3$	C$_1$–C$_3$
11	(bipy)Pt[CH$_2$CH$_2$CH$_2$]	2.030	2.665	2.037	1.534	1.534	
12	(PEt$_3$)$_2$Pt[CH$_2$CMe$_2$CH$_2$]	2.080	2.698	2.086	1.535	1.536	
13	(PPh$_3$)$_2$Pt[C(CN)$_2$CH$_2$C(CN)$_2$]	2.137	2.71	2.139	1.545	1.584	2.404
14	(PPh$_3$)$_2$Pt[C(CN)$_2$CH(Ph)C(CN)$_2$]	2.14	2.69	2.16	1.56	1.55	2.39
15	(PPh$_2$)$_2$Pt[C(CN)$_2$CH(Ph)C(CN)CO$_2$Et)]	2.16	2.69	2.20	1.56	1.51	2.40
16	Cl$_2$Py$_2$Pt[CH$_2$CH$_2$CH$_2$]	2.04	2.69	2.19	1.48	1.82	2.55
17	Cl$_2$Py$_2$Pt[CH(Ph)CH(Ph)CH$_2$][a]	2.06	2.60	2.11	1.59	1.48	2.39
		2.05	2.62	2.17	1.59	1.71	2.60
18	Cl$_2$Py$_2$Pt[CH$_2$C(Me)(CH$_2$OH)CH$_2$]	2.042	2.676	2.039	1.542	1.548	
19	Cl$_2$(bipy)Pt[CH$_2$CH$_2$CH$_2$]	2.07			1.63		
20		2.057		2.093	1.625	1.546	
21		2.011		2.097	1.587	1.547	
22		2.074		2.054	1.535	1.537	
23		2.071		2.074	1.532	1.528	
24		1.97		2.05			2.37

[a] Phenyl groups are trans to one another. Two independent molecules are present within the unit cell.

Table 37. Bond Angle (deg) Data for Platina(II)- and Platina(IV)cyclobutanes

entry	C_1-M-C_3	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral[a]	ref(s)	entry	C_1-M-C_3	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral[a]	ref(s)
11	69.9	98.8	95.5		0.0	175,176	18	70.15	98.75	95.55	95.54	1.0	79
12	67.3	97.5	95.4	95.1	22.4	119	19	71.9	96.2	96.0		0.0	175
13	68.4	100.4	93.5	92.3	24.4	103	20	70.0	97.3	94.7	95.7		188
14	67.7	100.9	92.3		28.6	101	21	69.8	97.2	96.7	94.6		188
15	66.9	103.2	91.2		29.7	101	22	68.8	98.8	94.8	95.5		96
16	74.2	100.9	99.3	84.3	12.5	41	23	68.7	99.8	94.7			92
17	70	102	90	91	28	187	24					11.0	66
	76	104	91	84	22								

[a] The angle formed between the planes of C_1-M-C_3 and $C_1-C_2-C_3$.

Table 38. Bond Length (Å) Data for Ruthena(II)-, Irida(III)-, Pallada(II)-, and Platina(II)cyclobutanones

entry	complex	$M-C_1$	$M-C_2$	$M-C_3$	C_1-C_2	C_2-C_3
25	$(PMe_3)_4Ru[CH_2COCH_2]$	2.217		2.222	1.468	1.449
26	$(PPh_3)_2(CO)ClIr[CH_2COCH_2]$	2.169	2.561	2.184	1.48	1.50
27	$(PPh_3)_2Pd[CH(CO_2Me)COCH(CO_2Me)]$	2.135	2.389	2.165	1.467	1.492
28	$(AsPh_3)_2Pd[CH(CO_2Me)COCH(CO_2Me)]$	2.125	2.384	2.152	1.482	1.473
29	$(bipy)Pd[CH(CO_2Me)COCH(CO_2Me)]$	2.103	2.374	2.085	1.471	1.471
30	$(PPh_3)_2Pt[CH(CO_2Me)COCH(CO_2Me)]$	2.133	2.416	2.155	1.470	1.493
31	$(PPh_3)_2Pt[CH(COMe)COCH(COMe)]$	2.183	2.486	2.153	1.496	1.491
32	$(PPh_3)_2Pt[CH_2COCH_2]$	2.145	2.422	2.119	1.473	1.496
33	$(AsPh_3)_2Pt[CH(Ph)COCH(Ph)]$[a]	2.116	2.350	2.187	1.50	1.47
34	$(AsPh_3)(t\text{-}BuNC)Pt[CH(CO_2Me)COCH(CO_2Me)]$[b]	2.057	2.509	2.121	1.509	1.492

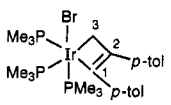
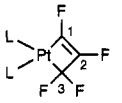
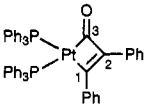
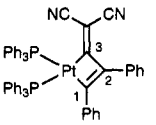
[a] Both Ph groups occupy equatorial positions. [b] One substituent is equitorial; the other, axial. C_3 is trans to $AsPh_3$.

Table 39. Bond Angle (deg) Data for Ruthena(II)-, Irida(III)-, Pallada(II)-, and Platina(II)cyclobutanones

entry	C_1-M-C_3	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral[a]	ref(s)
25	65.72	110.8	83.5	83.5	45.6	133
26	66.5	106.6	87.1	86.0	41.0	161
27	68.5	109.5	80.8	79.2	53.2	157
28	68.7	109.5	80.6	79.9	52.3	157
29	68.8	107.1	81.2	81.8	51.3	157
30		108.8	82	80.7	50.4[b]	154
31	67.3	107.2	82.8	84.0	48	159,160
32	68.4	107.7			51	162
33	69.2	110.4	79.0	77.2	56.7	163
34	68.1	102.6	88	86.1	42	158

[a] The angle formed between the planes of C_1-M-C_3 and $C_1-C_2-C_3$. [b] Reported in ref 155 as 49.7°.

Table 40. Bond Length (Å) Data for Irida(III)- and Platina(II)-cyclobutenes

entry	complex	$M-C_1$	$M-C_2$	$M-C_3$	C_1-C_2	C_2-C_3	C_1-C_3
35		2.134		2.166	1.344	1.525	
36		2.039		2.08	1.35	1.47	
37		2.08		2.09	1.45	1.31	
38							

wise to the metal species. Even a lengthening due to polarization cannot explain this increase over the respective free cyclopropane bond distances of 1.501 to 1.524 Å.

Tables 38 and 39 include the bond lengths and bond angles of structurally characterized metallacyclobutanones. The most notable feature of these complexes is the large pucker angle, i.e. dihedral angle formed between the planes derived from C_1-M-C_3 and $C_1-C_2-C_3$, which ranges from 41° to 56.7°. Organic cyclobutanones are only slightly nonplanar with dihedral angles of 0−10°. Therefore, the significant puckering of metallacyclobutanones has been attributed to a considerable transannular attraction between the metal and C_2 carbonyl group which shortens the $M-C_2$ distance substantially. In fact, the extent of nonplanarity and the decreased $M-C_2$ bond distance has led investigators to suggest that the bonding description of these molecules should include contribution from an (η^3-allyl)metal species **30** shown previously.

The dihedral angle of platina(II)- and (IV)cyclobutanes found in Table 37 ranges from 0.0° to 29.7°. The formation of the planar structures is attributed to the bidentate bipyridyl ligand coordinated to the metal in entries numbered 11 and 19. The most highly puckered platina(II)- and (IV)cyclobutanes, entries 14, 15, and 17, each have a phenyl substituent at the C_2 position suggesting a possible transannular attraction between the metal and the phenyl bearing carbon, albeit smaller than found in the metallacyclobutanones described above.

A few structures of metallacyclobutenes and metallacyclobutabenzenes have been determined and their data is reported in Tables 40−43. The data is consistent with a metallacyclic structure showing considerable shortening of the olefinic C_1-C_2 bond as expected.

IV. Chemistry of Metallacyclobutane Derivatives

A. Reactions Yielding Alkane Products

The formation of alkanes from metallacyclobutanes has been reported for Ni(II), Pd(II), Rh(III), Pt(II),

Table 41. Bond Angle (deg) Data for Irida(III)- and Platina(II)cyclobutenes

entry	C_1-M-C_3	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral[a]	ref
35	72.98	99.2			5.5	168
36	65.8	104.7	97.5		0.0	110
37	62	100	101	97		107
38	63	101			23	109

[a] The angle formed between the planes of C_1-M-C_3 and $C_1-C_2-C_3$.

Table 42. Bond Length (Å) Data for Rhoda(III)-, Nickela(II)-, and Platina(II)cyclobutabenzenes

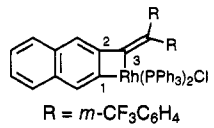
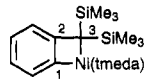
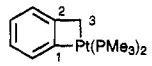
entry	complex	M–C1	M–C2	M–C3	C1–C2	C2–C3
40	 R = *m*-$CF_3C_6H_4$	1.984		2.030	1.395	1.480
41		1.897		2.075	1.38	1.534
42		2.060		2.122	1.38	1.52

Table 43. Bond Angle (deg) Data for Rhoda(III)-, Nickela(II)- and Platina(II)cyclobutabenzenes

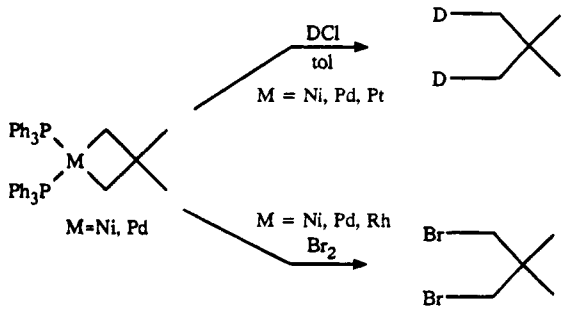
entry	C_1-M-C_3	$C_1-C_2-C_3$	$M-C_1-C_2$	$M-C_3-C_2$	dihedral[a]	ref
39	66.2	99.3	99.5	94.6	0.0	116
40	71.7	106.0	96.9	85.3		114
41	66.7	104.6	97.6	90.8		178

[a] The angle formed between the planes of C_1-M-C_3 and $C_1-C_2-C_3$.

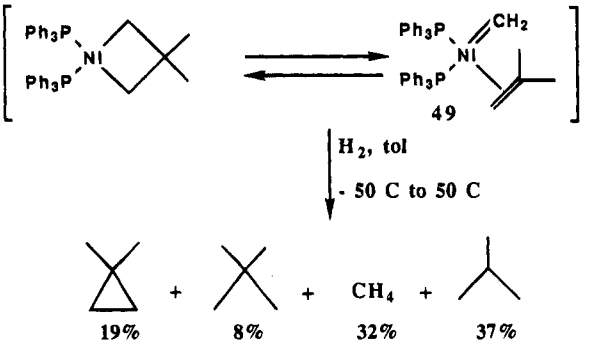
and Pt(IV) complexes. Oxidative addition of 2 mol of DCl in toluene to the 2,2-dimethylmetallacyclobutanes of Ni(II) and Pd(II) results in quantitative formation of 1,3-dideuterium-substituted neopentane (Scheme 11).[122] The same substitution pattern was observed for the analogous reaction of DCl in D_2O with 2,2-dimethylplatina(II)cyclobutanes.[117,121] Similarly, treatment of the nickela(II)- and pallada(II)-cyclobutanes, as well as a rhodium analogue,[125] with Br_2 leads to formation of 1,3-dibromo-2,2-dimethylpropane in 49%, 67%, and 37% yield respectively (Scheme 11). These reactions presumably proceed by oxidative addition of the reagent to the metal, followed by reductive elimination of substituted neopentane. It is interesting that 2 mol of DCl are required and that 1-deuterio-3-chloroneopentane is not produced.

When 2,2-dimethylnickela(II)cyclobutane is pyrolyzed in the presence of hydrogen by raising the temperature from −50 to 50 °C, the products shown in Scheme 12 result.[122,189] (Reported yields are per Ni.) Although the 2,2-dimethylpropane and 1,1-dimethylcyclopropane result from hydrogenolysis and reductive elimination followed by reductive elimination, respectively, the production of the dominant alkane species, methane and isobutane, is believed to result from a nickel–carbene intermediate **49**. In contrast, the dominant products from hydrogenolysis of the Pd(II) analogue were neopentane (69%) and dimethylcyclopropane (14%) with only small amounts

Scheme 11

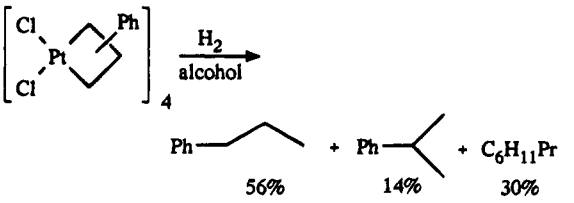


Scheme 12



of methane and isobutane (4% and 6%, respectively) formed.

When platina(IV)cyclobutane tetramers are shaken in alcohol in the presence of gaseous hydrogen, a variety of alkane products result.[61] One example is shown in eq 47 and Table 44 displays other hydrogenolysis products. In each case a mixture of isomeric



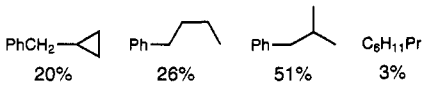
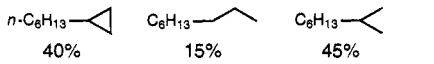
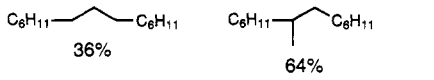
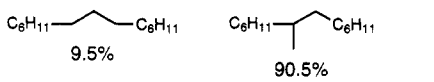
(47)

alkane products results. It has not been determined, however, whether isomerization occurs within the platina(IV)cyclobutane to create an isomeric mixture of tetramers which upon hydrogenolysis yield the isomeric alkanes or whether isomerization to the observed alkane products occurs during hydrogenolysis from one tetrameric species.[47,75]

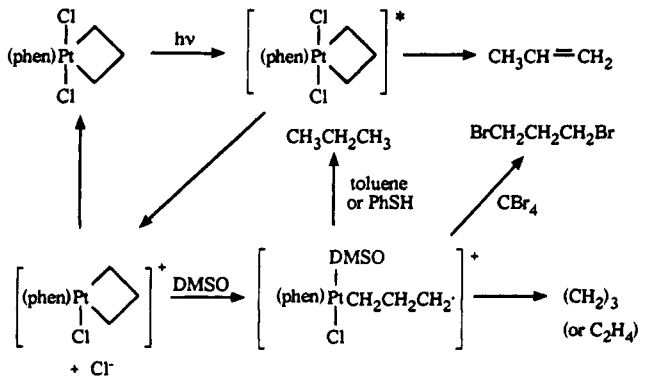
Under certain solvent and additive conditions, it is possible to produce alkanes photolytically from platina(IV)cyclobutane, albeit cyclopropanes and alkenes are the dominant products.[190,191] For example, the photolysis of (1,10-phenanthroline)dichloroplatina(IV)cyclobutane in CH_2Cl_2/thiophenol yields about 26% propane. The same reaction performed in DMSO/thiophenol or DMSO/toluene yields 5% propane and 1% propane, respectively. A solvent mixture of DMSO/CBr_4 produced 1,3-dibromopropane in small, yet detectable, amounts. The proposed reaction pathway for this photolytic process is illustrated in Scheme 13.

The thermal reaction of platina(IV)cyclobutane, run in the presence of diphenylphosphines, also forms propane in varying yields.[83] The example shown in eq 48 is the highest yielding of all the reaction

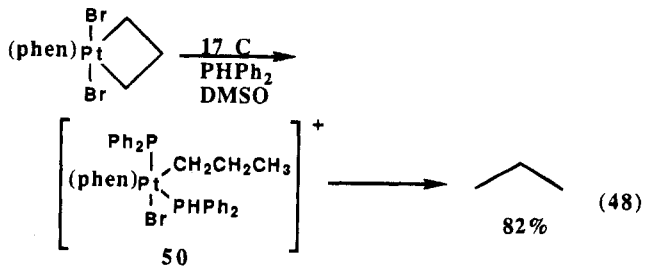
Table 44. Hydrogenolysis Products of Mono- and Disubstituted Platina(IV)cyclobutane Tetramers

R	products
CH_2Ph	
n-C_6H_{13}	
trans-1,2-diphenyl	
cis-1,2-diphenyl	

Scheme 13



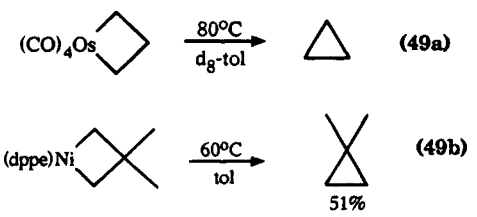
conditions tested. Other phosphines were added also and were found to generate little or no propane product. The success of diphenylphosphine in generating propane is presumably due to the successive transfers of the phosphine hydrogen from the coordinated phosphine to hydrocarbon and intermediate **50** is thereby proposed.



(48)

B. Reactions Yielding Cyclopropane Products

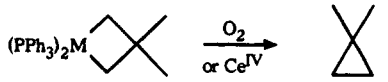
Reductive elimination of metallacyclobutanes to form cyclopropane is facilitated by numerous reagents as well as heat and light. Osmia(II)- and nickela(II)cyclobutanes both decompose to cyclopropanes and other alkene or alkane products when heated according to eqs 49a[174] and 49b.[122,189]



(49a)

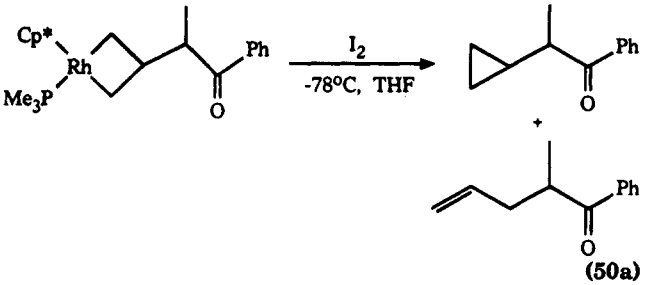
(49b)

The oxidative decomposition of 2,2-dimethylnickela(II)- and -pallada(II)cyclobutane with O_2 or Ce^{IV} yields 1,1-dimethylcyclopropane in 80% to 87% yields as illustrated in equation 49c.[122]

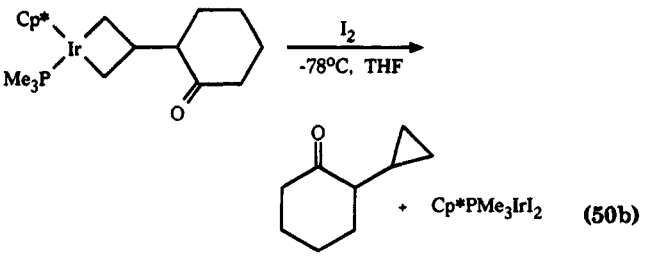


(49c)

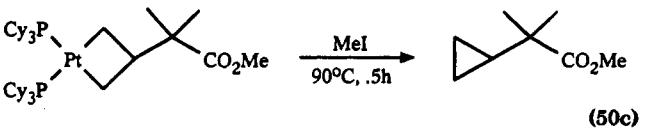
Addition of I_2 in THF at −78 °C causes rhoda(III)- and irida(III)cyclobutanes to reductively eliminate forming substituted cyclopropanes (eqs 50a and 50b).[136,142] Similarly, reaction of platina(II)cyclobutane with methyl iodide at 90 °C forms a cyclopropane product (eq 50c).[139] Presumably all three of



(50a)



(50b)



(50c)

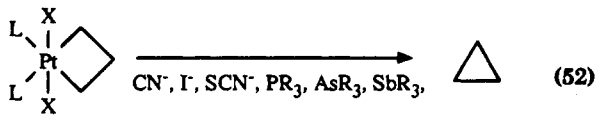
these reactions involve oxidative addition of the iodine with subsequent reductive elimination of the cyclopropane moiety. Since these metallacycles were prepared by nucleophilic attack at the central carbon of a π-allyl−rhodium, −iridium, or −platinum complex, respectively, the overall scheme provides an alkylative cyclopropanation protocol.

The 2,2-dimethylplatina(II)cyclobutane, shown in eq 51, forms 1,1-dimethylcyclopropane upon reaction with I_2, Br_2, and NCCN, as well as with heating.[117,121]

(51)

Equation 52 illustrates the most common reagents invoked for reductive elimination of cyclopropane from platina(IV)cyclobutane tetramers and monomers.[37,39,41,61,62,65,73,82,83,85,88,89,190-192] The anionic ligands CN^-, I^-, and SCN^- as well as the tertiary phosphine, arsine, stibene, and sulfur donor ligands, all exhibit high trans influence. The facility of these electron-rich ligands in reductive elimination is due to their

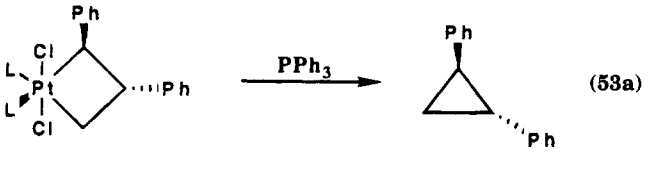
ability to replace the existing coordinated ligand, L. Therefore a stronger ligand, such as PR_3, liberates cyclopropane faster than a weaker ligand. However, the rate of reductive elimination also depends on the halide and ligand originally on the platina(IV)-cyclobutane.



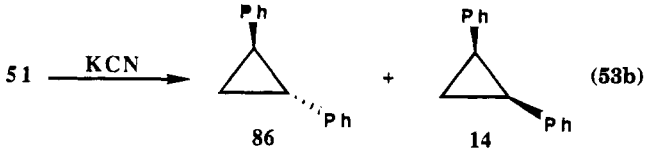
(52)

X= Cl, Br
L= Nitrogen donor ligands, THF

Another interesting feature of these reactions is the resulting stereochemistry of the cyclopropane product. Addition of triphenylphosphine to dichlorobis(pyridyl)*trans*-1,2-diphenylplatina(IV)cyclobutane (**51**) yields *trans*-1,2-diphenylcyclopropane with complete retention of stereochemistry (eq 53a). However, when **51** is treated with KCN, a mixture of *trans*- and *cis*-1,2-diphenylcyclopropane isomers result in an 86:14 ratio, respectively (eq 53b). This result indicates that trans to cis isomerization occurred during reductive elimination suggesting a possible ionic intermediate for this process, in contrast to the concerted mechanism proposed for reductive elimination resulting from the addition of PPh_3.[73]

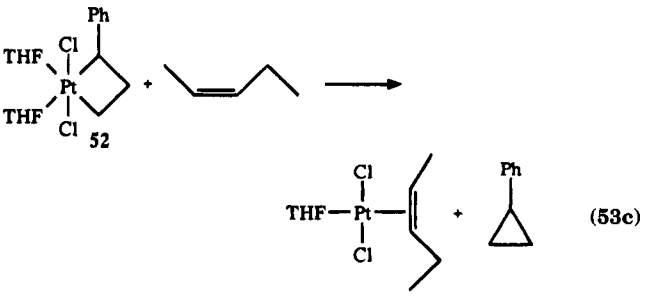


(53a)



(53b)

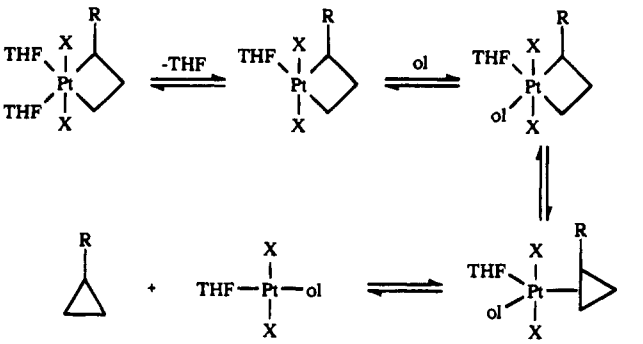
Other reagents that reportedly induce reductive elimination of platina(IV)cyclobutanes include $LiAlH_4$, H_2O, and CO.[61,62,90] Displacement of cyclopropanes by olefins also occurs as is illustrated in eq 53c for the reaction of **52** with 2-pentene.[61,65,193,194] An



(53c)

olefin exhibits high trans effect but low trans influence. Therefore, the generation of cyclopropane is slower than for the ligands previously described and does not occur if the platina(IV)cyclobutane monomer bears stronger coordinated ligands such as pyridine. However, olefins can cause reductive elimination of cyclopropane from platina(IV)cyclobutane tetramers or monomers in solution with a weak coordinating

Scheme 14



solvent, such as THF. The proposed pathway for this process is shown in Scheme 14.[193]

Thermal and photolytic decomposition of platina(IV)cyclobutanes also generate cyclopropane, along with other alkane and alkene products.[41,74,82,83,89,90,190,191,195,196] Platina(IV)cyclobutane monomers bearing high trans influence ligands yield cyclopropane in the highest yields when heated. For example, more than five times as much cyclopropane is generated upon heating a platina(IV)cyclobutane where L = ethylenediamine than when L = pyridine due to the higher trans influence of the former. The thermal reaction of platina(IV)cyclobutanes bearing bidentate ligands also generated cyclopropane when run in the presence of phosphines. Cyclopropane yields varied from 1% to 77% depending on the temperature, the solvent, and the type of phosphine added.

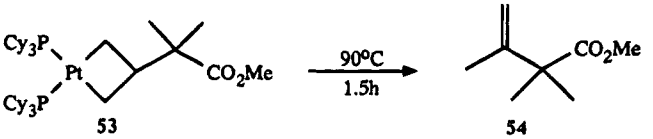
The photodecomposition of platina(IV)cyclobutanes also varies with reaction conditions (solvent and additive) to produce cyclopropane, propene, and ethylene products. The highest yield of cyclopropane formed by photolysis reportedly results from the reaction shown in eq 54.[191]

(54)

C. Reactions Yielding Olefinic Products

By far, this is the predominate reaction of metallacyclobutanes. The formation of free alkene species from metallacyclobutanes has been reported for Ni(II), Pt(II), and most commonly Pt(IV). Equation 49b in the previous section illustrates the thermal decomposition of a 2,2-dimethylnickela(II)cyclobutane to 1,1-dimethylcyclopropane. This reaction also yields the olefinic products ethylene, 2-methylpropene, and 3-methyl-1-butene in 14%, 27%, and 3% yield (per Ni) respectively.[122,189]

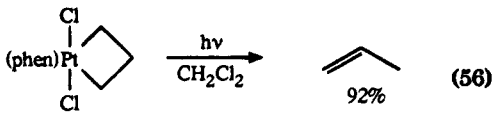
The thermal decomposition of **53** in dimethoxyethane–benzene-d_6 forms the olefinic product **54** exclusive of cyclopropane (eq 55).[139] The β-hydride elimination and subsequent reductive elimination of



(55)

the olefin is apparently a lower energy pathway than C–C bond formation to yield cyclopropane.

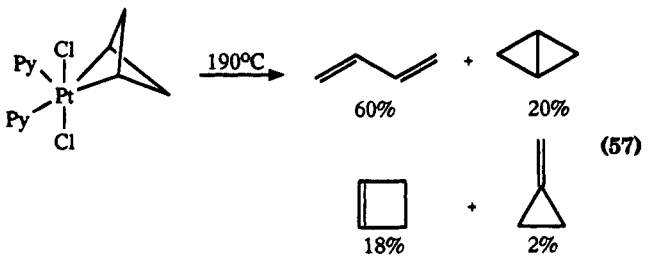
Both thermal and photolytic decomposition of unsubstituted platina(IV)cyclobutanes form propene, along with other products, as illustrated in eq 56.[39,41,74,82,83,190,196] In this example propene is formed



(56)

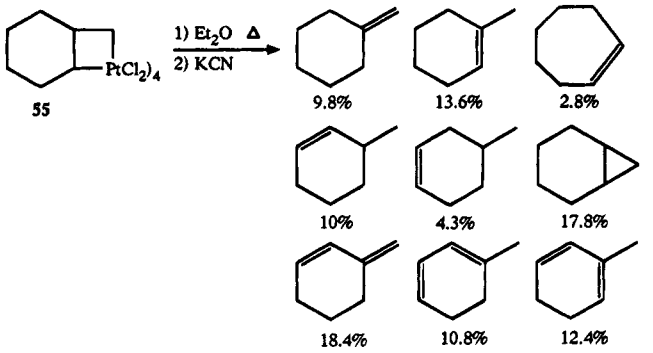
in 92% yield. However, by changing solvent, ligands, temperature, and other additives, the distribution of products easily can be affected to yield larger amounts of ethylene, cyclopropane, and other products. For example, ethylene can be formed in yields up to 70% if the decomposition conditions include DMSO or CH_3CN solvents in the presence of tertiary phosphines.[74,83]

Other platina(IV)cyclobutane systems can form free alkenes. Equation 57 demonstrates the thermal decomposition of a cis-1,3-disubstituted platina(IV)-cyclobutane to three different olefinic products.[90]



(57)

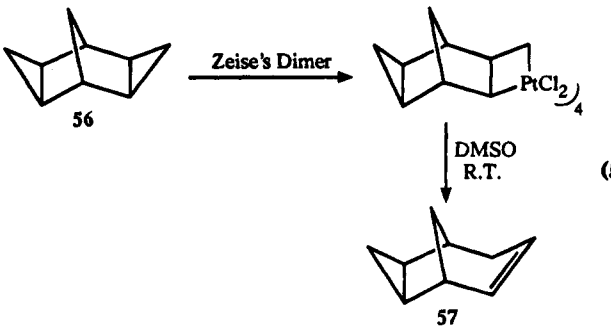
The cis-1,2-disubstituted platina(IV)cyclobutane tetramer **55** forms eight different olefinic products, along with the reductive elimination product, when heated in diethyl ether followed by addition of KCN (eq 58).[89] The same product distribution is observed



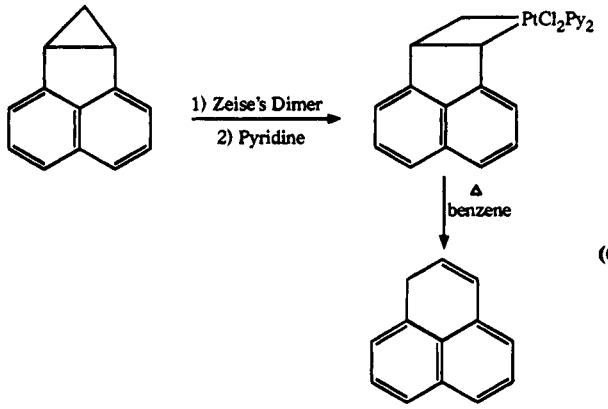
(58)

when bicyclo[4.1.0]heptane is heated in the presence of platinum(II), suggesting a platina(IV)cyclobutane intermediate for the latter process. Obviously, not all of these products are primary as there is ample opportunity for subsequent isomerization.

A ring homologated olefinic product results when **56** reacts with Zeise's dimer to form a platina(IV)-cyclobutane tetramer which subsequently is treated with DMSO at room temperature (eq 59).[197,198] Another example of this ring homologation technique is shown in eq 60.[94] Both of these reactions are suggested to proceed via an intermediate in which the platinum has rearranged into the disubstituted



(59)

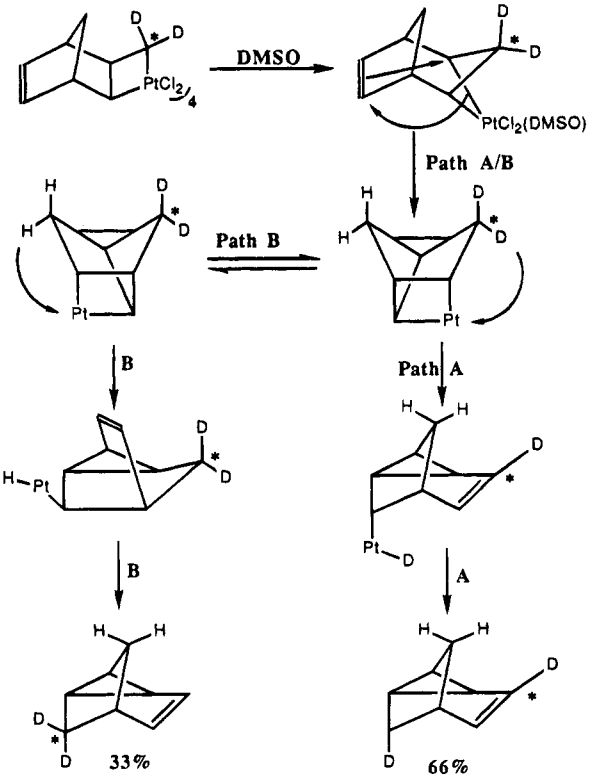


(60)

C–C bond of the cyclopropane moiety. A β-hydride abstraction step, followed by reductive elimination, then leads to the observed products.[199] However, recent evidence in the author's laboratory suggests that simple β-hydride abstraction is not the pathway.

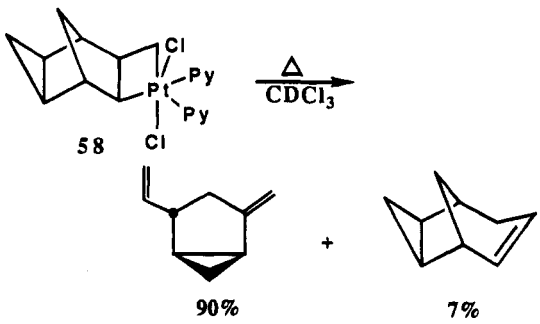
When the deuterium- and ^{13}C-labeled unsaturated norbornyl platina(IV)cyclobutane tetramer undergoes a ring homologation process, two isomers result. Scheme 15 illustrates the observed products and the

Scheme 15



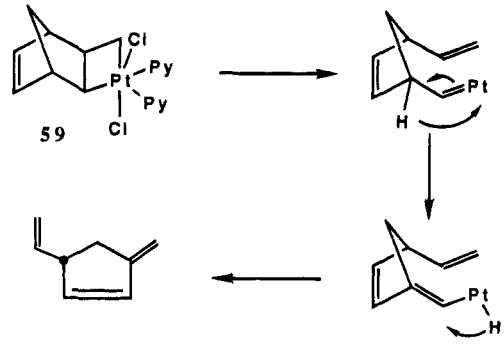
detailed mechanism proposed for this reaction.[200] Path A is suggested to yield 66% of the reaction product, while path B is responsible for 33% of the product. The same reaction, utilizing a Rh(I) catalyst, results in the same nortricyclic system. However, ^{13}C labeling shows that only path A is followed.[94,201] This suggests that rhodium inserts into the more substituted bond and does not rearrange as platinum does.

When **58** and **59** are heated in $CDCl_3$, five-membered ring dienes result along with the ring-expanded product (eq 61 and Scheme 16).[198] The



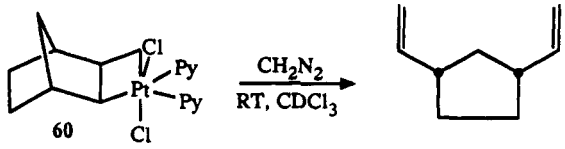
(61)

Scheme 16

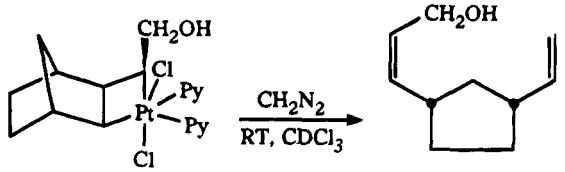


proposed pathway for the formation of the diene complex invokes cleavage of the platina(IV)cyclobutane moiety to form a platinum–carbene olefin complex which subsequently undergoes hydrogen rearrangement followed by reductive elimination to the observed olefinic product as shown in Scheme 16.

cis-1,3-Divinylcyclopentyl ring systems result when **60** is treated with diazomethane at room temperature (eq 62a).[76,198] This procedure has been performed on 1,2,3-trisubstituted platina(IV)cyclobutanes to form *cis*-divinylcyclopentanes with stereospecificity (eq 62b).[96] A trans stereochemistry result may be obtained from the epimer of the substrate in eq 62b.[96]

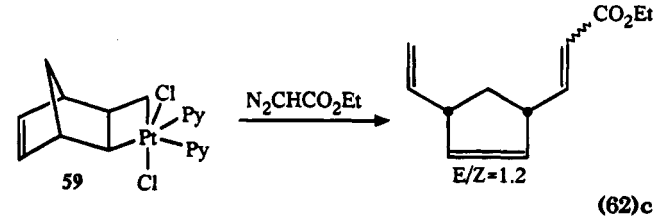


(62a)



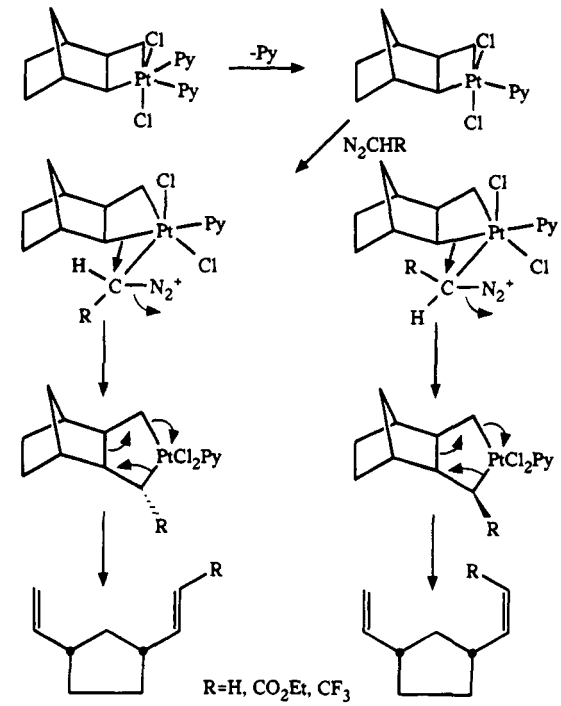
(62b)

The utility of this reaction is the stereochemical control that can be achieved at one double bond and the two allylic centers. The reaction shown in eq 62c was studied with hopes of achieving stereochemical control at the second double bond as well.[92] However, reaction of **59** with ethyl diazoacetate results in formation of both the *E* and *Z* isomers of the carbethoxy-substituted divinyl product. Scheme 17 illustrates the proposed mechanism for the reactions shown in eqs 62a, 62b, and 62c.[92]

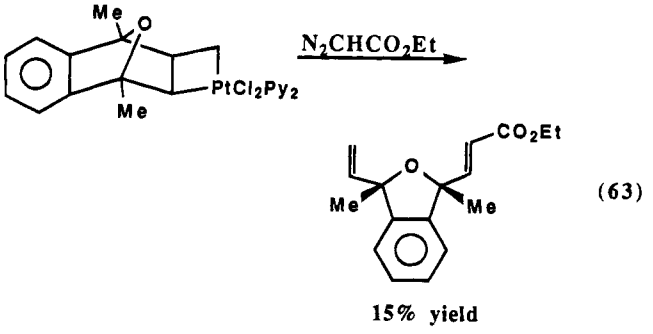


(62)c

Scheme 17



There are a couple of interesting features in this reaction. The effective diazo reagent is limited to those that are somewhat electron deficient. That is, the three reagents shown work nicely, but, for example, diazoethane and phenyldiazomethane yield only reductive elimination to the original cyclopropane substrate. Further, substituents at the C-1 position have little effect on the product stereochemistry (*E*/*Z* ratio = 1.4) save the substrate in reaction 62b and diazoacetic ester. In this case, the *E*/*Z* ratio is 0.7 and is best explained by an interaction of the hydroxymethyl moiety with the incoming diazoacetic ester.[92b] Finally, if a substituent (Me) is placed at the bridgehead, as is shown in eq 63, the stereochemistry of the diene product is exclusively trans.[92c] This result provides corroborating evidence in support of the pathway shown in Scheme 17 in that by virtue of the fact that the methyl group at the bridgehead modulates the reaction, the diazoderivative must be attacking the platinum at the site indicated.

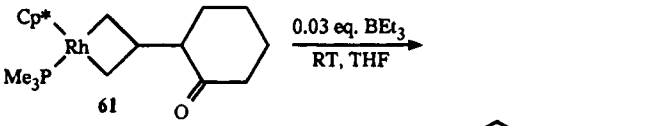


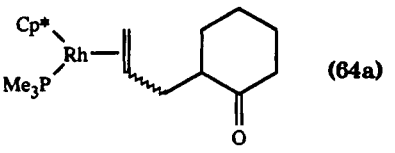
(63)

15% yield

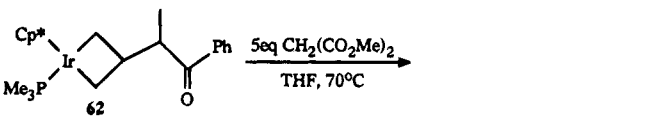
D. Reactions Yielding Alkene–Metal Complexes

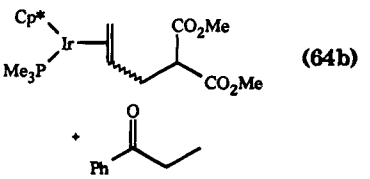
In many instances, olefins are produced as described in the previous section but often the metal complexes to the olefin and reduces its recoverability due to loss in volatility. The most recent examples of metallacyclobutanes reacting to form metal–olefin complexes are shown in eqs 64a and 64b.[136] Equation





(64a)



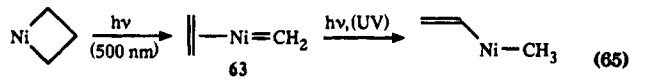


(64b)

64a illustrates the mild Lewis acid, Et_3B, catalyzed rearrangement of rhoda(III)cyclobutane **61** to a mixture of stereoisomers of the rhodium(I)–olefin complex. The irida(III)cyclobutane **62** however, does not rearrange to an iridium(I)–olefin complex under similar conditions presumably due to stronger metal–carbon bonding. It is possible though to form an iridium–alkene complex by heating **62** in the presence of excess dimethyl malonate.

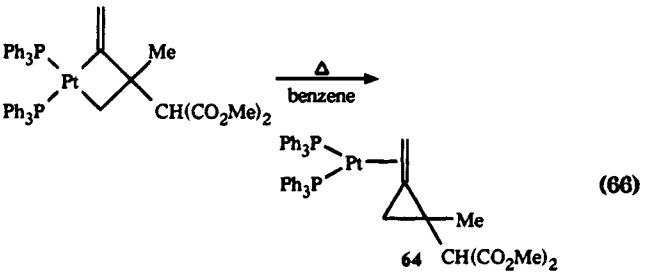
The metallacycles **61** and **62** are formed by nucleophilic attack at the central carbon of the respective metal π-allyl complex. The mechanism for alkene–metal complex formation is suggested to result from reversible dissociation of the enolate from the metallacycle to form the π-allylic complex, followed by nucleophilic attack at the terminal carbon of the π-allyl complex. The reversible nature of this reaction was amply demonstrated in the case of iridium by the crossover substitution.

If the unligated nickela(II)cyclobutane in eq 65 is irradiated at $\lambda \geq 500$ nm, a methylidenylnickel ethylene complex **63** is formed. Upon further irradiation with UV light, **63** rearranges to a vinylnickel methyl species.[106]



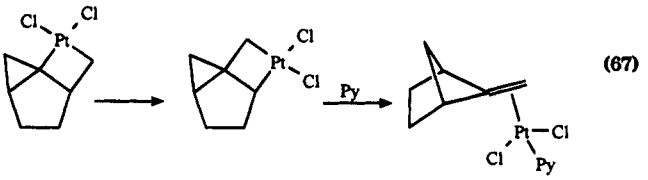
(65)

The unusual vinylidene-substituted platina(II)-cyclobutane readily reductively eliminates methylenecyclopropane to form the Pt(0)–olefin complex **64** as shown in eq 66.[138]



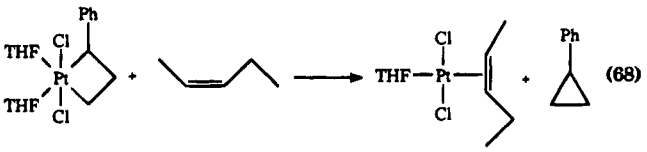
(66)

The platina(IV)cyclobutane, shown in eq 67, reportedly undergoes a skeletal rearrangement to form a bicyclic platinum(II)–olefin complex.[95] This example is one of a few which support the concept that platina(IV)cyclobutanes may react via carbocationic intermediates.



(67)

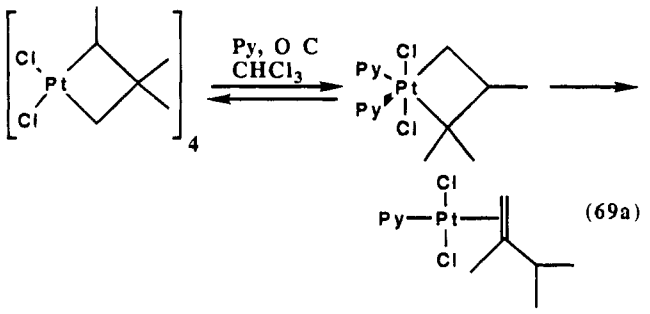
As previously shown in eq 53b, platina(IV)cyclobutanes can react with olefins to reductively eliminate the cyclopropane moiety and form a Pt(II)–olefin species.[61,65,193,194] The example is repeated in eq 68. The olefin either can replace a weak ligand attached to the monomeric platina(IV)cyclobutane, as shown, or react directly with the tetrameric species.

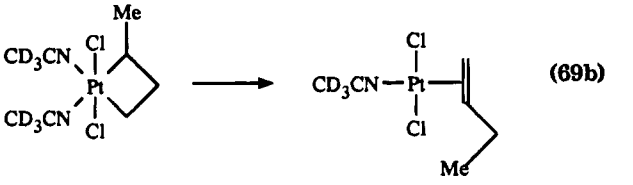


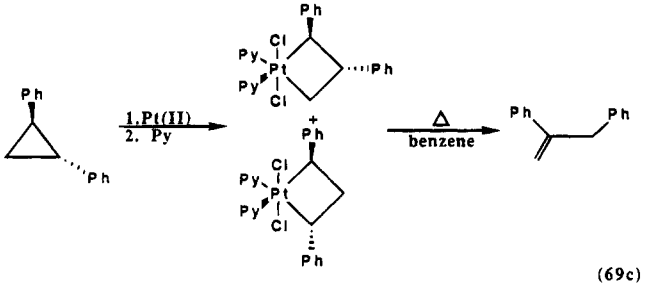
(68)

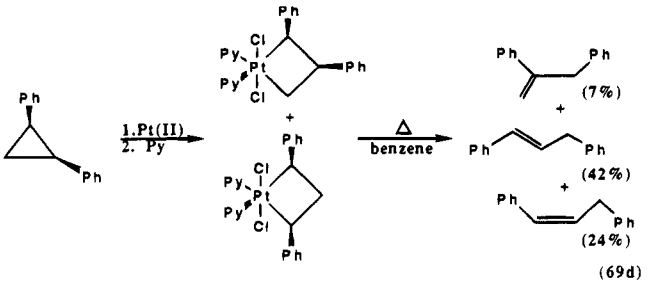
Pt(II)–olefin complexes also result from direct isomerization of tetrameric platina(IV)cyclobutanes (eq 69a). As shown below, it is necessary for the reaction to proceed via a Puddephatt rearrangement prior to the hydride transfer process leading to product. This concept, thermodynamic complex rearranging to a less stable complex followed by irreversible product formation, is a common theme for reaction of platina(IV)cyclobutane complexes. Platina(IV)cyclobutanes bearing weakly coordinated or bulky nitrogen donor ligands also easily isomerize to the Pt(II)–olefin complex as illustrated in eq 69b.[71,74,80,202–205]

Another interesting set of examples is shown with *cis*- and *trans*-stilbene derivatives. The trans isomer leads exclusively to the methylene product from a mixture of platinacycles and the cis isomer yields mostly chain homologation products from a mixture of platinacycles.[94] This is one of the few examples







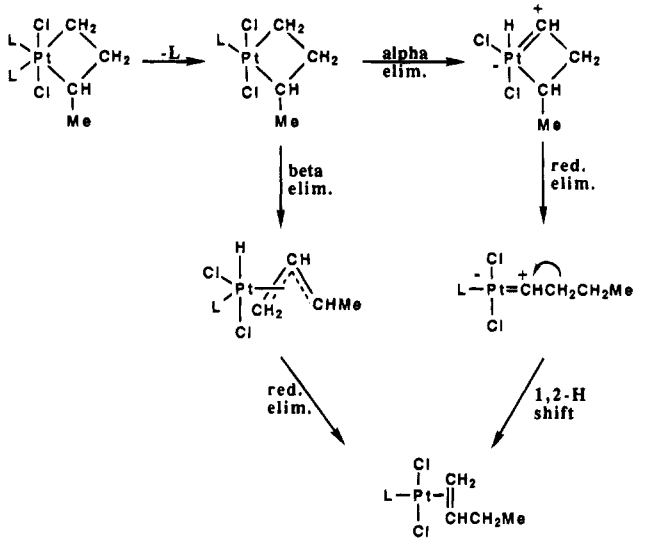


where stereochemistry around the olefinic product has been noted.

The mechanism of platina(IV)cyclobutane isomerization to Pt(II)–olefin complexes has been investigated previously and remains somewhat speculative. Scheme 18 illustrates two possible pathways for this reaction involving either an initial α- or β-hydride elimination.[199] Although there has been some controversy over the correct pathway, the most recent findings by Puddephatt support an initial α-hydride elimination rather than the β-hydride elimination pathway.

This is one of the few mechanistic pathways in metallacyclobutane chemistry that has been explored. Further elaboration is necessary. First of all, with platinum(IV) complexes, it is important to remember that a Puddephatt rearrangement can occur yielding a reactive isomer other than that which is isolated or observed. While it is readily assumed in many organometallic reactions that initial β elimination is the main pathway for olefin formation, it is not the case in platinum(IV)cyclobutanes. It appears, in this case, that a sequence: α-hydride transfer → reductive elimination → β(1,2)-hydride transfer is the correct pathway. Another

Scheme 18



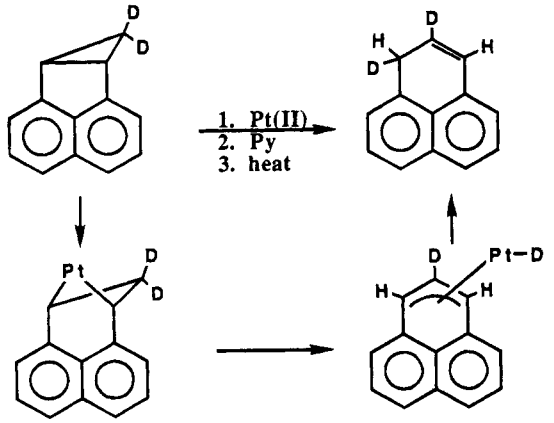
scenario is α-hydride transfer followed by a β- or 1,2-hydride transfer with subsequent reductive elimination. It is clear from labeling experiments that a hydrogen atom is transferred from carbon 1 to carbon 3 and from 2 to 1.

It is assumed that the α hydride is transferred to the metal but there is no evidence for this intermediate complex. Further, the π component of the alkylidenyl intermediate has been shown to be polarized platinum minus and carbon plus, lending credence to the β- or 1,2-hydride transfer in the final step.[70b] Thus, this reaction may appear to be a simple β elimination process, but it is not. It is the authors' suggestion that other systems exhibiting β elimination characteristics be investigated thoroughly to make sure that they are not part of a cascade effect initiated by an α-hydride transfer.

Finally, the intriguing question arises as to why these systems do not conform to the typical β-hydride elimination scenario. First of all, due to the ring system, it is not possible to attain coplanarity between the elements Pt–C–C–H_β which is usually required. The most obvious option is a transannular interaction whereby the β hydrogen is transferred to the platinum and the carbon system collapses to a π allylic complex. There is no evidence for this option but it is possible to at least conceive of either a filled or an unfilled orbital on platinum(IV), d^6, pointing directly at the atom in question. The following system, eq 70, was designed to test this transannular interaction concept and to find new ways for ring homologation which will be discussed in a subsequent section.[94] If the β-transannular hydride transfer pathway is followed in this reaction, a primary deuterium kinetic isotope effect would be anticipated. The fact is that there is no kinetic isotope effect. This suggests that the transannular hydride transfer concept is not an option in this system. However, the Puddephatt rearrangement necessary to get the bicyclic intermediate may actually be the rate-limiting step.

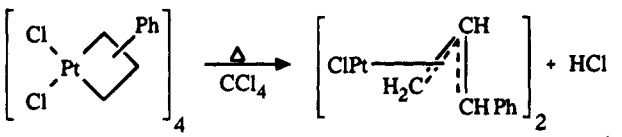
E. Reactions Yielding π-Allyl–Metal Complexes

An π-allyl–platinum(II) complex has been reported when the phenyl-substituted platina(IV)cyclobutane tetramer was refluxed in CCl_4 according to eq 71.[61]



(70)

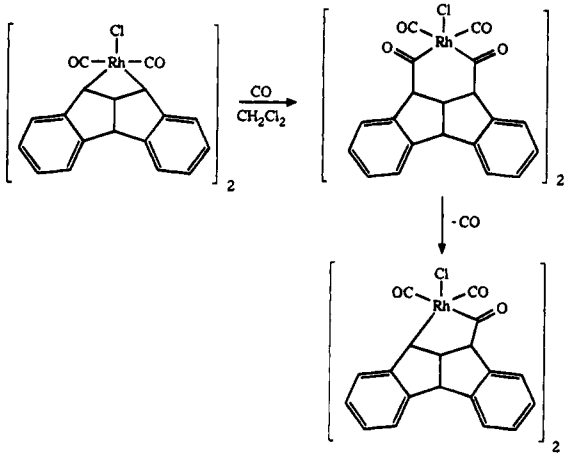
Other examples of π-allyl–platinum(II) complex formation from the reaction of certain cyclopropanes with Zeise's dimer suggest a platina(IV)cyclobutane intermediate; however, the metallacycle has not been detected.[62,71]



(71)

F. Reactions Yielding Ring-Expanded Products

Ring-expanded products have been formed from reactions of Rh(III), Ni(II), Pt(II), and Pt(IV) metallacyclobutane derivatives. When carbon monoxide is added to a rhoda(III)cyclobutane dimer, CO insertion yields a rhoda(III)cyclohexadione dimer. Evaporation to dryness forms a rhoda(III)cyclopentanone dimer (eq 72).[105]

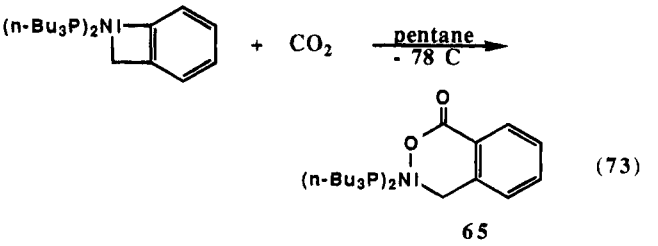


(72)

Nickela(II)cyclobutabenzene provides a carbon dioxide capturing reagent at −78 °C to form the six-membered cyclic carboxylate **65** in high yield (eq 73).[112] A ring-expanded product also results when the platina(II)cyclobutanone, shown in eq 74, reacts with 2 mol of hexafluoroacetone.[155]

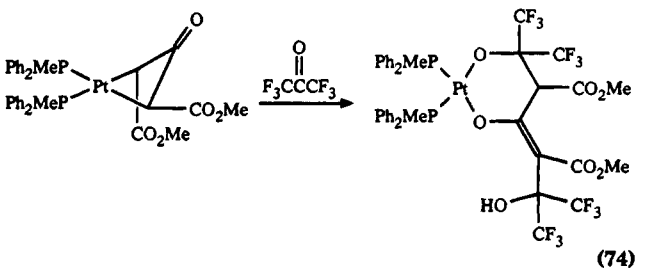
A platina(II)cyclopentanone product results when the platina(II)cyclobutane **66** is stirred in acetonitrile under 1 atm of carbon monoxide (eq 75). Similarly, exposure of **67** to 1 atm of sulfur dioxide leads to the SO_2 insertion product (eq 76).[175]

Platina(IV)cyclopentanes have been synthesized by ring expansion of platina(IV)cyclobutane derivatives

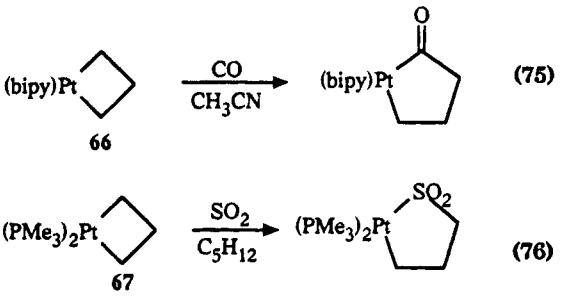


(73)

65



(74)



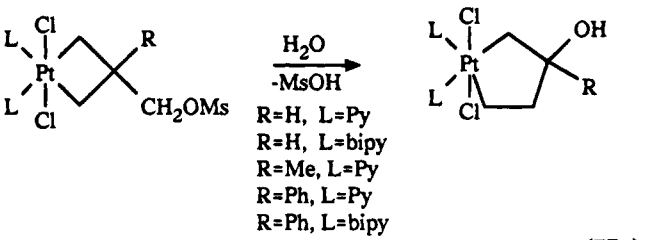
66

(75)

67

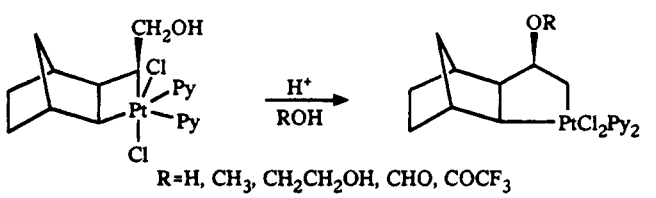
(76)

via a carbocationic pathway similar to the well-known cyclopropyl carbinyl cation mechanism. The solvolysis of platina(IV)cyclobutanes bearing mesylate esters produces platina(IV)cyclopentanol products according to eq 77a.[78,79] The reaction pathway shown in Scheme 19 supports both the kinetic and labeling studies performed on this reaction. Again, it is important to note the platinacyclic rearrangement that accompanies this process.



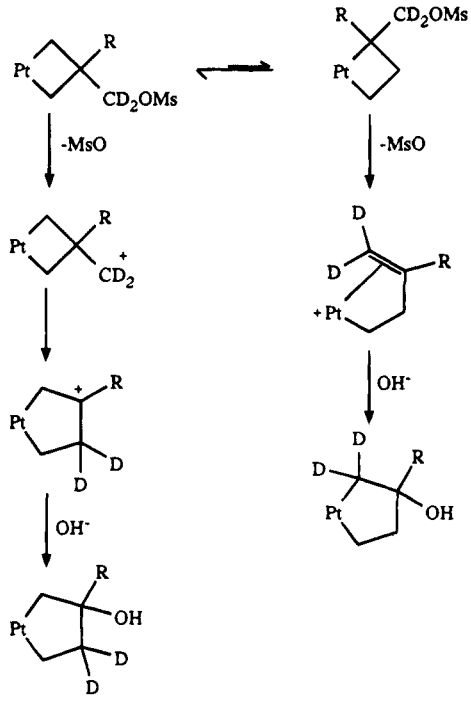
(77a)

A similar reaction, eq 77b, was run on a more substituted system to determine the stereospecificity of the process which would provide additional evidence for the pathway, especially for the cationic pi complex. In this case, acid catalysis was used to effect the cationic center.

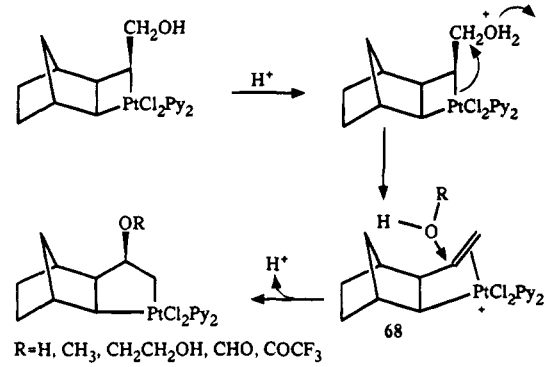


(77b)

Scheme 19



Scheme 20



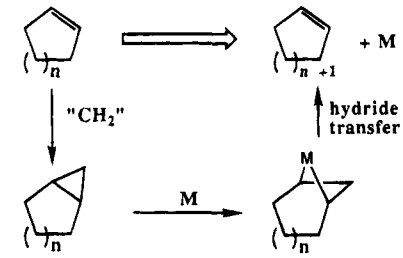
R=H, CH_3, CH_2CH_2OH, CHO, $COCF_3$

The suggested mechanistic pathway is shown as Scheme 20.[76,81,206] This ring expansion process is both regio- and stereospecific. The regiospecificity is believed to result from intermediate **68** in which formation of the cyclopentane derivative is clearly favored over the cyclobutane complex. The stereospecificity is also proposed to result from nucleophilic attack of **68** at the olefinic face anti to the platinum functionality. If the epimer of the reactant in eq 77b is used, the epimeric product is obtained (i.e., the OR moiety is down). Thus, the stereospecifically proposed π complex is held tightly to the cationic platinum and nucleophilic attack is always on the olefinic face opposite to the one bound to platinum. Further elaboration of this reaction for general alkene hydration has not occurred.

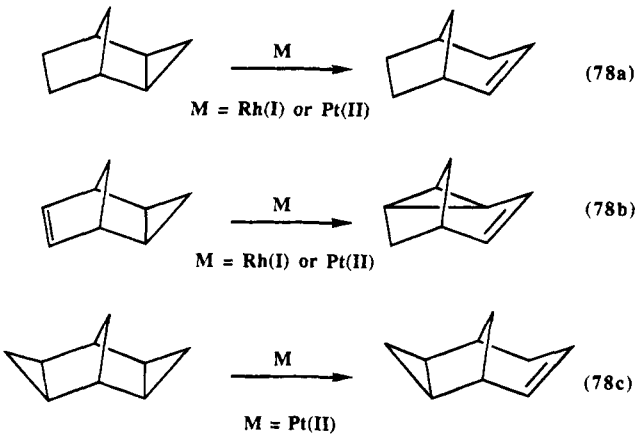
G. Reactions Yielding Hydrocarbon Ring- and Chain-Homologated Products

Another variation on the previous theme involves the possibility of ring or chain homologation. The idea is derived from Scheme 21 using a generic system: Thus, the metal must insert directly into the ring juncture bond or rearrange into said bond followed by the hydride-transfer processes discussed earlier.

Scheme 21



Early work demonstrated that this process was viable in the norbornyl series as shown in eqs 78a, 78b, and 78c.[97] While the rhodium case is catalytic,



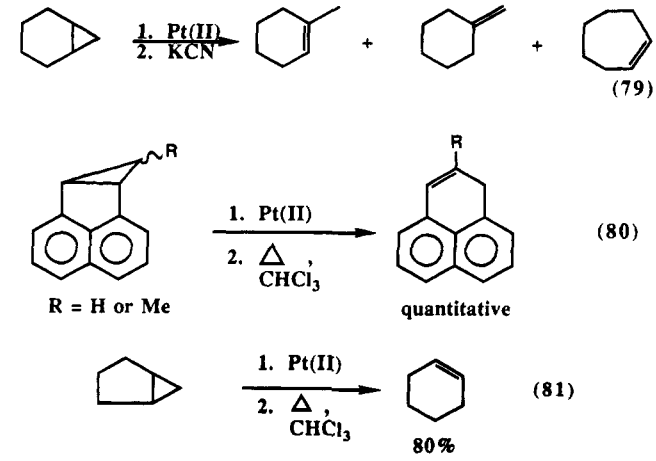
(78a)

(78b)

(78c)

the platinum system is not. Presumably, the driving force for this transformation is ring strain. Incidentally, the mechanistic pathway in eq 78b is not the same for rhodium and platinum, as was discussed in Scheme 15.

With simpler systems, the early results were not encouraging (eq 79). More recent results are, however, encouraging (eqs 80 and 81). The six-membered



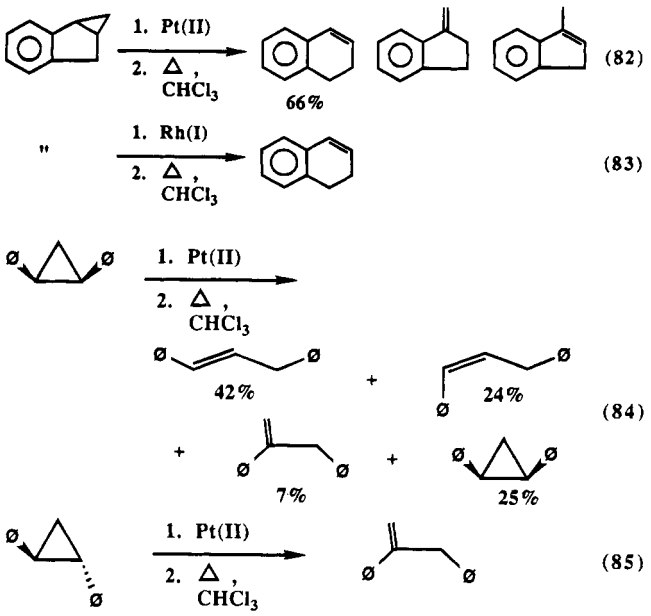
(79)

(80)

(81)

ring is thought to resist ring expansion due to steric interactions between the required platinum position and the puckered ring residues. This steric problem is relieved in the systems shown as eqs 80–82.

In acyclic substrates such as those shown in eqs 84 and 85, the stereochemistry of the substrate determines the result. In the cis substrate, the reactive metal can be accommodated in the more substituted bond and hydride transfer is facile. This is not the case with the *trans*-stilbene analogue. The two

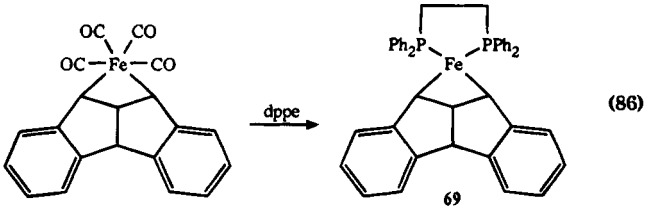


chain homologated olefinic products in eq 84 are apparently derived from a choice of the two β hydrogens.

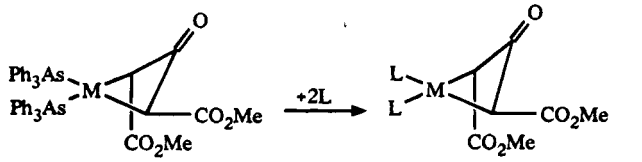
Two final points: (1) Equation 82 shows platinum giving three products with the major one being the ring expanded and desired result. However, rhodium yields only the ring-homologated product, eq 83. Thus, it appears that both metals wish to choose the more substituted bond but platinum can isomerize out, whereas rhodium does not. (2) It may be possible to entice the metal into the desired bond with carefully placed chelating moieties as part of the substrate.

H. Reactions Yielding Ligand Exchange Products

A labile ligand bound to the metal of a metallacyclobutane can be displaced by a variety of less labile ligands to create new metallacyclobutanes. The ferretane molecule reacts with 1,2-bis(diphenylphosphino)ethane (dppe) to yield **69** (eq 86).[104]



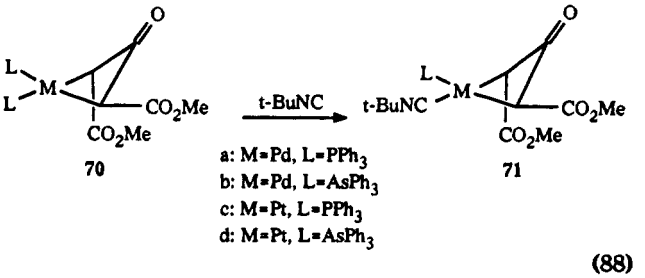
Pallada(II)- and platina(II)cyclobutanones bearing labile $AsPh_3$ ligands react with various phosphorus ligands and 2,2′-bipyridine to yield the metallacyclobutanones shown in eq 87.[158] However, these metallacyclobutanones can be prepared directly, Table 9.



M=Pd, L= PPh_3, bipy
M=Pt, L= PPh_3, $PMePh_2$, PMe_2Ph, dppe

(87)

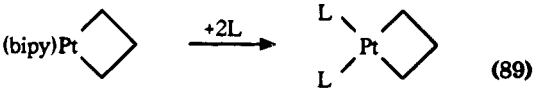
An equimolar proportion of *tert*-butyl isocyanide can displace one $AsPh_3$ or PPh_3 ligand from **70a–d** to form a high yield of the interestingly substituted complexes **71a–d** (eq 88).[158] If the triphenylarsine



(88)

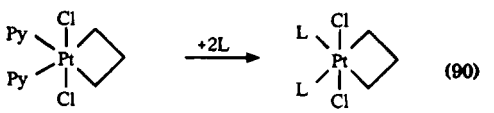
complexes **70b** and **d** are further treated with PPh_3 in dichloromethane at room temperature, displacement of $AsPh_3$ occurs to form **71a** and **c**. Furthermore, under forcing conditions, triphenylphosphine can displace both the $AsPh_3$ and *t*-BuNC of **71b** and **d** to form the bis(triphenylphosphine) derivatives.

Ligand substitution of the labile 2,2′-bipyridyl ligand on the platina(II)cyclobutane, shown in eq 89, occurs readily by the monodentate ligands PPh_3, PEt_3, and PMe_3, and to a lesser degree by *t*-BuNC.[175,176] This facile substitution contrasts with the inert behavior, under comparable experimental conditions, of the coordinatively saturated platina(IV)cyclobutane, $Cl_2(bipy)Pt[CH_2CH_2CH_2]$.



L=PMe_3, PEt_3, PPh_3, t-BuNC

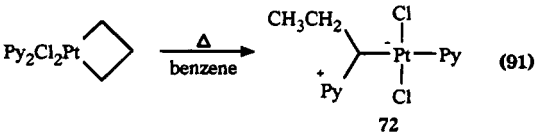
When phosphorus ligands are added to platina(IV)cyclobutanes reductive elimination occurs. However, labile oxygen and nitrogen donor ligands on platina(IV)cyclobutanes can be displaced by other nitrogen donor ligands according to eq 90.[41,65,195,207]



L= d_5-Py, 4-Mepy, bipy, en, phen

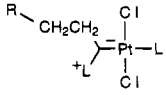
I. Reactions Yielding Ylide Products

During the early investigations of platina(IV)cyclobutane chemistry, it was discovered that upon refluxing in benzene, dichlorobis(pyridyl)platina(IV)cyclobutane formed a bright yellow isomeric solid.[39] The X-ray crystal structure later revealed the formation of the ylide complex, dichloro(pyridinium)propylide)pyridineplatinum(II) (**72**) (eq 91).[41,208] Reaction



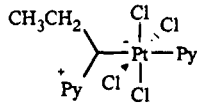
of the platina(IV)cyclobutane with CCl_4 in chloroform formed the analogous tetrachloro product **73**, which

Table 45. Platinum(IV) Ylide Complexes



L	R	ref
py	H	41,80
py	Me	74,80
py	Et	80
py	Bu	74
py	Me_2	47,204
2-Mepy	Me	47,74
2-Mepy	Bu	47,74
2-Mepy	Ph	47,204
2-Mepy	p-tol	47
2-Mepy	Me_2	47
3-Mepy	H	41
4-Mepy	H	41

also can be synthesized by addition of $CCl_4/CHCl_3$ to **72**.[40,41,208] This type complex suggests fairly clearly

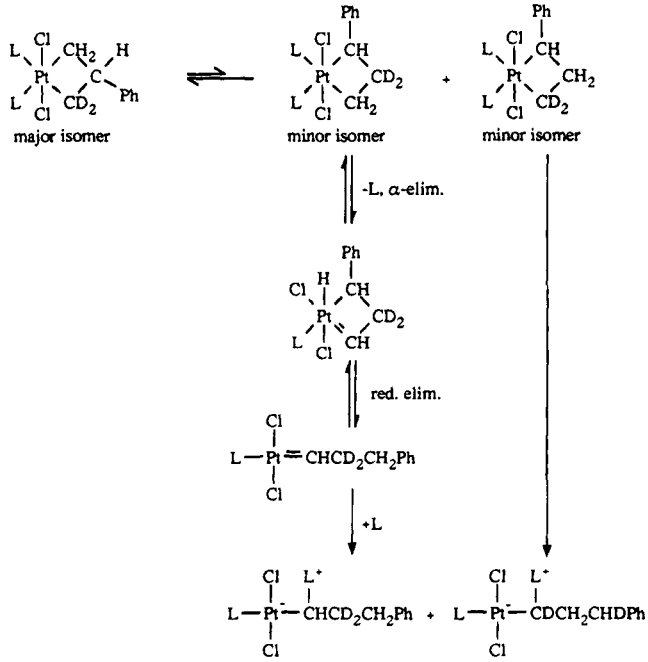


73

that the alkylidene π component is polarized platinum minus and carbon plus.

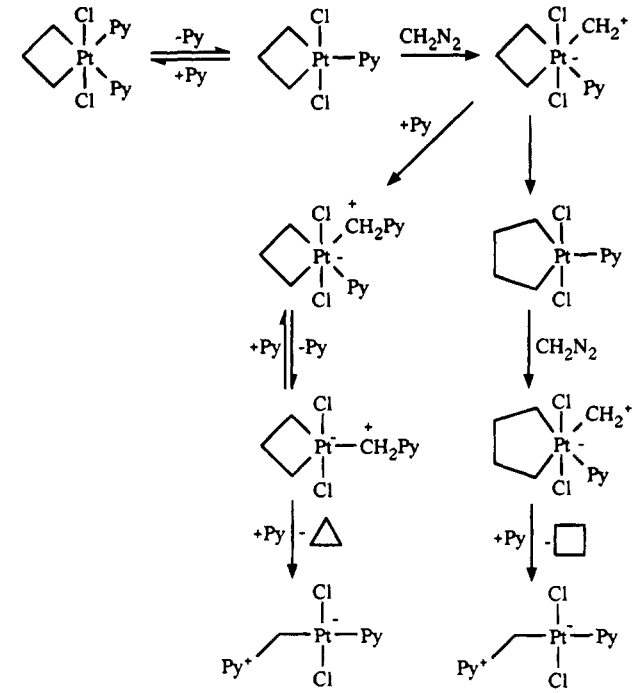
Substituted platinum ylide complexes can be formed by this methodology and are listed in Table 45. Of particular interest is the formation of only one ylide isomer although the parent platina(IV)cyclobutanes are known to exist as an equilibrium mixture of two isomers (see eqs 92 and 93). Labeling studies suggest that the reaction proceeds only from the minor or less thermodynamically stable platina(IV)cyclobutane isomer according to the pathway shown in Scheme 22.[204]

Scheme 22



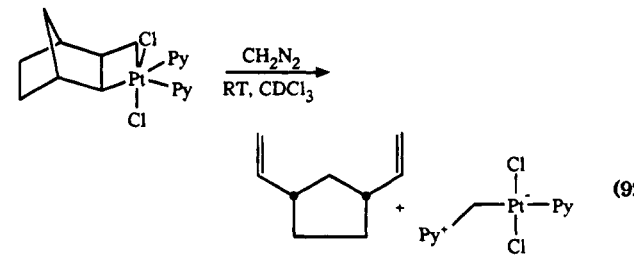
Photochemical methods also transform the minor platina(IV)cyclobutane isomer into ylide products.

Scheme 23



When the ligand on the platina(IV)cyclobutane is 2-Mepy the reaction can proceed at room temperature. Clearly, the steric hinderance caused by the *o*-Me group contributes to the relative ease of ylide formation by promoting initial ligand dissociation.

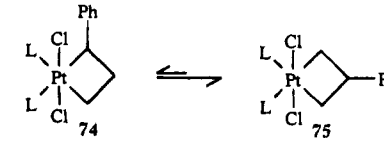
Platinum ylide complexes also have been synthesized from the reaction of norbornyl platina(IV)-cyclobutanes with diazomethane, although in low yields (eq 92).[198] The same ylide product results when an unsubstituted platina(IV)cyclobutane reacts with diazomethane. The proposed reaction pathway is illustrated in Scheme 23.[182] The partitioning between the two pathways shown in Scheme 23 seemingly is dependent on the platina(IV)cyclobutane starting material and the reaction temperature.



(92)

J. Intramolecular Rearrangement Yielding Isomeric Products

Platina(IV)cyclobutanes are known to undergo an unusual intramolecular rearrangement to form isomeric products (eq 93).[68] In the case of phenylcyclo-

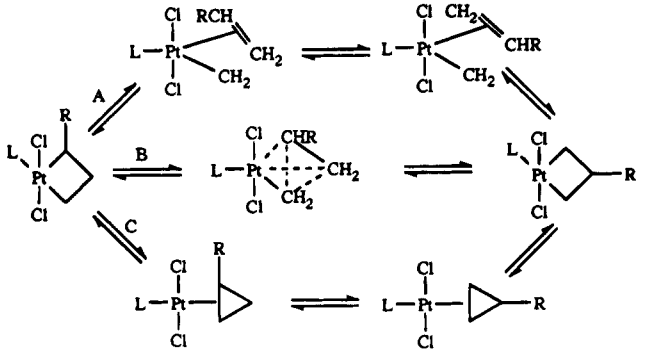


(93)

74 **75**

propane shown, the Pt(II) is believed to be inserted initially into the most highly substituted cyclopro-

Scheme 24



pane bond to form **74** which then isomerizes intramolecularly to **75**. The product ratio upon equilibration is 2.3 to 1, **75** to **74**[75] and occurs readily at room temperature indicating a low activation energy. The actual energy has not been determined.

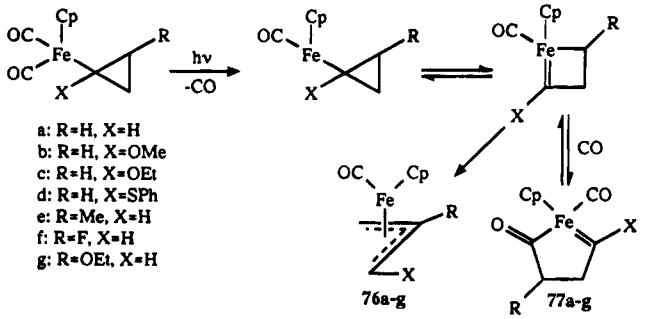
The above isomerization has been investigated extensively with various aryl and alkyl substituents on the platina(IV)cyclobutane, as well as numerous ligands. Three mechanisms have been proposed and are shown in Scheme 24.[68,72,75,207,209] However, the details of this rearrangement have been examined in a previous review so will not be described other than to state that the currently accepted pathway is that shown as B in Scheme 24.[47]

V. Metallacyclobutane Derivatives as Intermediates

A. Ferra(II)cyclobutane Derivatives as Intermediates

Ferra(II)cyclobutane and -cyclobutene intermediates have been proposed in a number of transformations involving iron complexes. Recently a ferra(II)-cyclobutene was proposed for reactions involving rearrangements of cyclopropanes σ bonded to iron.[170,171,210] Scheme 25 illustrates the role of ferra-

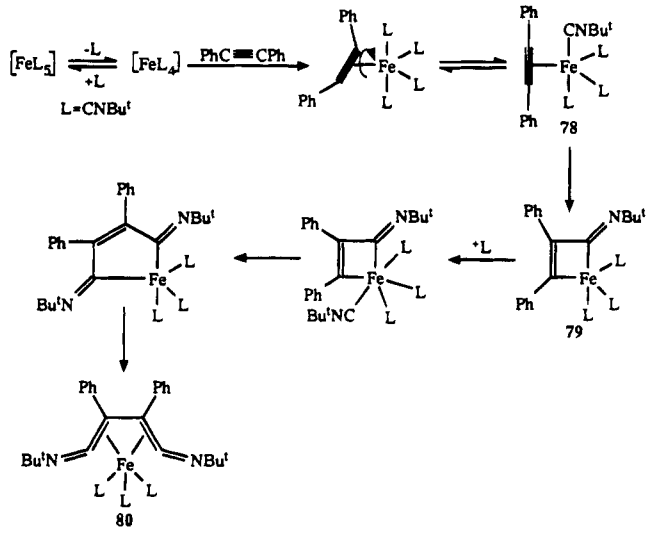
Scheme 25



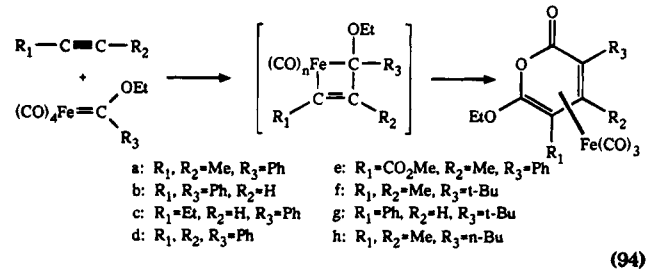
(II)cyclobutene in formation of both the π-allyl iron complex **76a–g** and the ferra(II)cyclopentenones **77a–g**. Although highly unstable, the proposed ferra(II)cyclobutene intermediate reportedly has been characterized by ^{1}H NMR spectroscopy.

The synthesis of a variety of 6-ethoxy-α-pyrone complexes by reaction of alkynes with (ethoxyalkylidene)tetracarbonyliron(0) complexes also is believed to occur via a ferra(II)cyclobutene intermediate ac-

Scheme 26



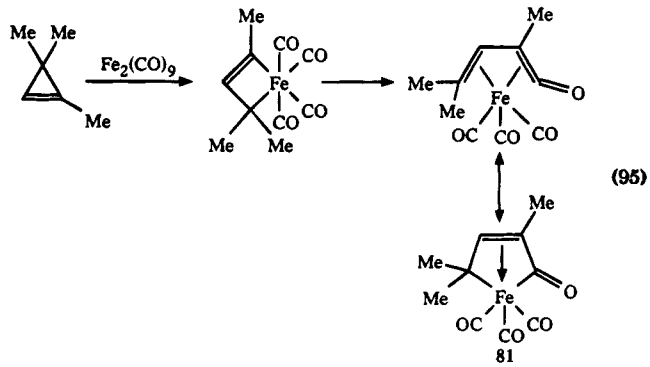
cording to eq 94.[211] Spectroscopic evidence also supports this key intermediate.



(94)

Another example of a proposed ferra(II)cyclobutene intermediate is shown in Scheme 26 for the formation of **80** from diphenylacetylene and pentakis(*tert*-butyl isocyanide)iron(0).[212] An oxidative cyclization reaction is believed to occur from the η^2-bonded acetylene **78** to form the metallacyclic intermediate **79**.

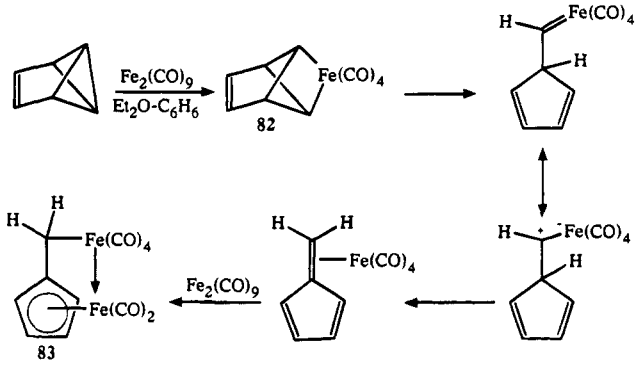
In the formation of **81**, a ferra(II)cyclobutene intermediate is believed to form by insertion of Fe(0) into the most highly substituted bond of 1,3,3-trimethylcyclopropene (eq 95).[213] Although having greater steric hindrance, this site may be favorable due to the increased electron density created by the methyl substituents. This conclusion appears tenuous and clearly needs additional support.



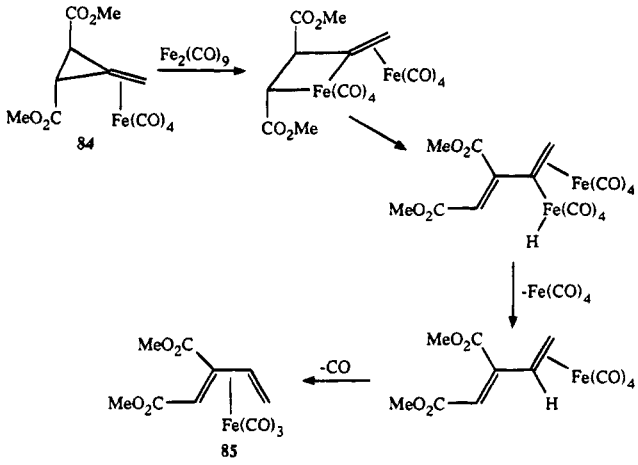
(95)

Two examples of proposed ferra(II)cyclobutane intermediates have been reported. Scheme 27 illustrates the transformation of benzvalene to hexa-

Scheme 27



Scheme 28



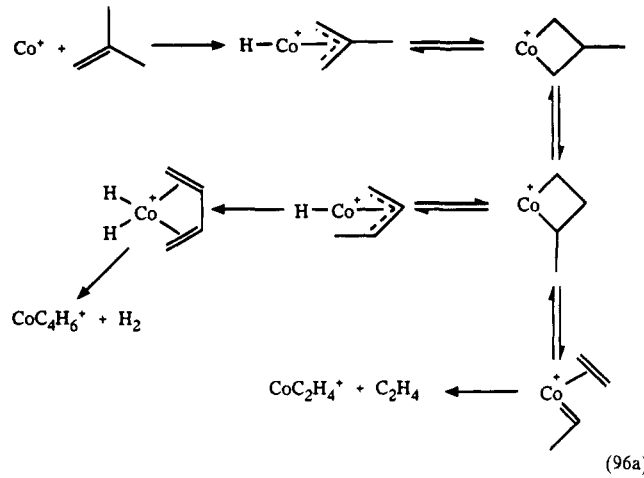
carbonyl fulvene diiron **83** via a unique and interesting ferretane intermediate **82**.[214]

The reaction shown in Scheme 28 involves oxidative addition of the strained sp^2-sp^3 bond of **84** to Fe(0) to form a ferra(II)cyclobutane intermediate which subsequently proceeds to give an interesting transformation as shown, **85**.[215] The trans-disubstituted starting material in Scheme 28 forms exclusively syn products. Likewise, the analogous cis-disubstituted starting material forms exclusively the anti product and also proceeds via a ferra(II)cyclobutane intermediate. It would be useful to determine where the hydrogens of **84** or the ferra(II)cyclobutane end up in the product. It is the β-hydride problem, again.

B. Cobalta(II)- and (III)cyclobutane Derivatives as Intermediates

Cobalta(III)cyclobutane intermediates have been proposed in reactions of cobalt ions with alkenes and cycloalkanes. Reaction of cobalt in the gaseous phase with 2-methylpropene yields the cleavage products ethylene and ethylene–cobalt complexes, as well the dehydrogenation product, $CoC_4H_6^+$. A cobalta(III)-cyclobutane ion intermediate was invoked to explain the cleavage results (eq 96a).[216] The isomerization of the metallacyclic intermediate is suggested to occur through either a cobalt–carbene intermediate or by a concerted process analogous to that proposed for the rearrangement of platina(IV)cyclobutanes shown in eq 93.

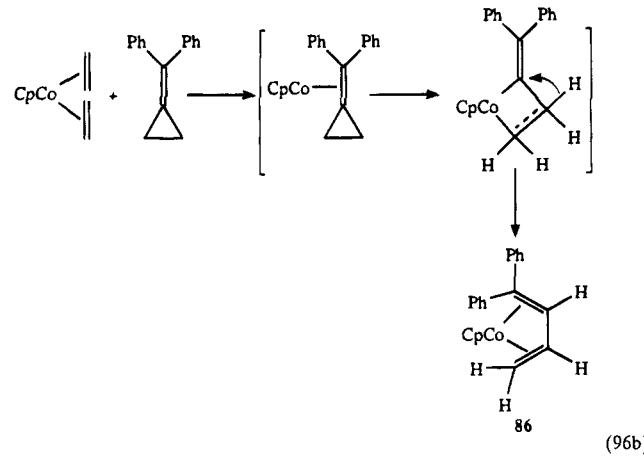
Further investigations of cobalt ion reactions with cyclopropanes, cyclobutane, and cyclobutanones also



(96a)

have led to suggestions of cobalt(III)cyclobutane ion intermediates.[179,180,217] Fe^+, Ni^+, and Rh^+ also were studied with the above organic substrates and metallacyclobutane intermediates again were proposed.[218,219]

In addition to reactions in the gas phase, a cobalta(II)cyclobutane intermediate was invoked in the reaction of CpCo-bis(ethylene) with (diphenylmethylene)cyclopropane to yield **86** (eq 96b).[220] Minor amounts of a binuclear cobaltacyclopentadiene product were observed.

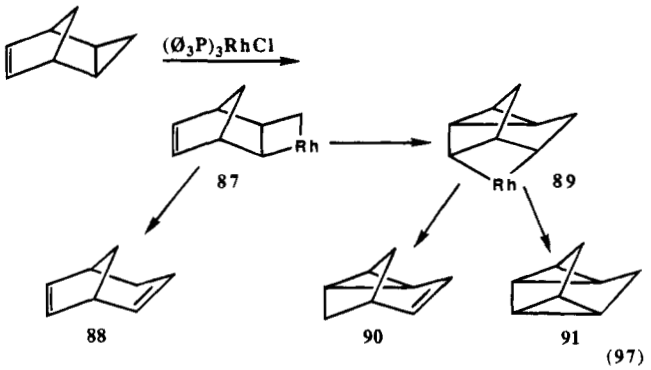


(96b)

C. Rhoda(III)cyclobutane Derivatives as Intermediates

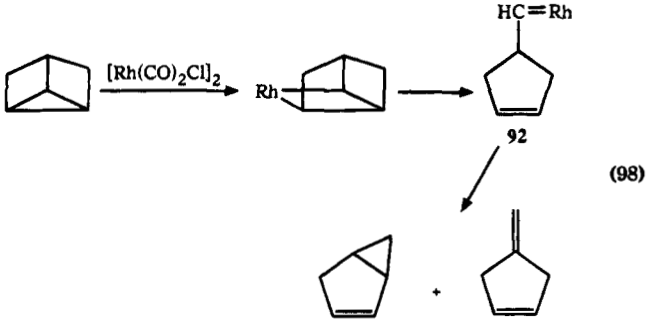
Rhodium(I)-catalyzed isomerizations of strained ring systems have been suggested to occur through a rhoda(III)cyclobutane intermediate. Intermediate **89** was proposed for the isomerization of *exo*-tricyclo-[3.2.1.$0^{2,4}$]octene to products **90** and **91** (eq 97).[201,221] A small percent of **88** also is produced in this isomerization but apparently follows an alternate pathway which is suggested to proceed via the rhoda(III)cyclobutane intermediate **87**.

A second example of a rhodium(I)-catalyzed isomerization containing a proposed rhoda(III)cyclobutane intermediate is shown as eq 98.[222] Tricyclo[2.2.0.$0^{2,6}$]-hexane is converted to 4-methylenecyclopentene via Rh(I) insertion into a carbon–carbon bond of the cyclopropyl moiety to form a rhoda(III)cyclobutane



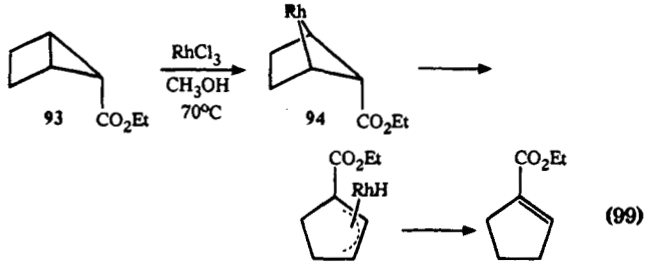
(97)

intermediate which rearranges to **92** before forming 4-methylenecyclopentene along with minor amounts of bicyclo[3.1.0]hex-2-ene.



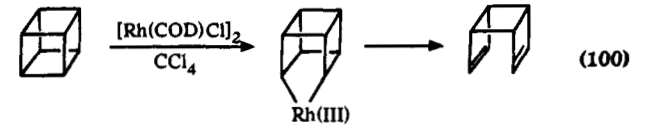
(98)

Substituted bicyclo[2.1.0]pentanes are proposed to catalytically isomerize to cyclopentenes via a rhoda(III)cyclobutane intermediate. The example shown in eq 99 produces 1-carbethoxycyclopentene, along with minor amounts of 3-carbethoxycyclopentene.[223] The metallacyclic intermediate **94** is formed by oxidative addition of the central carbon bond of **93** to the rhodium center.

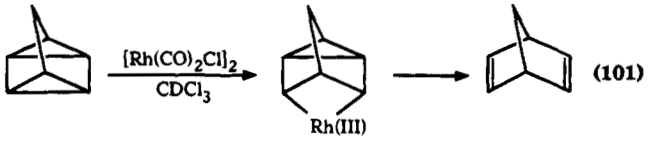


(99)

The Rh(I)-catalyzed valence isomerizations of cubane and quadricyclane derivatives to form *syn*-tricyclooctadiene and norbornadiene are shown in eqs 100[224] and 101,[225] respectively. Both isomerizations are suggested to proceed via a rhoda(III)cyclobutane intermediate as shown.

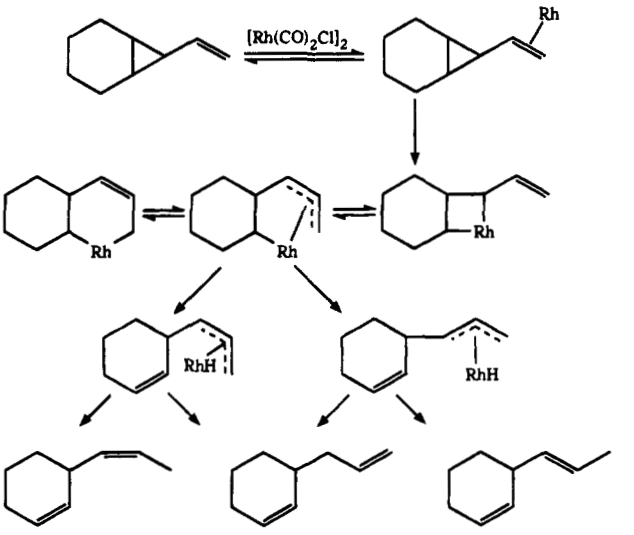


(100)

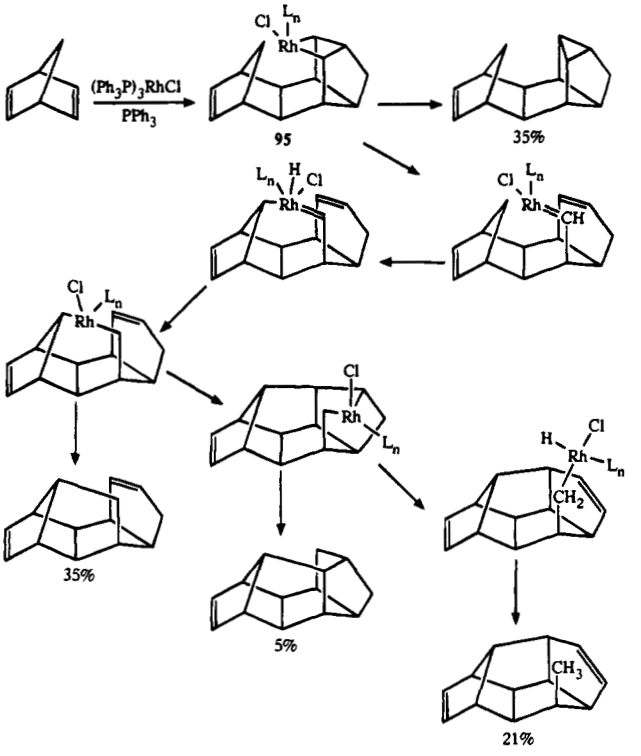


(101)

Scheme 29



Scheme 30

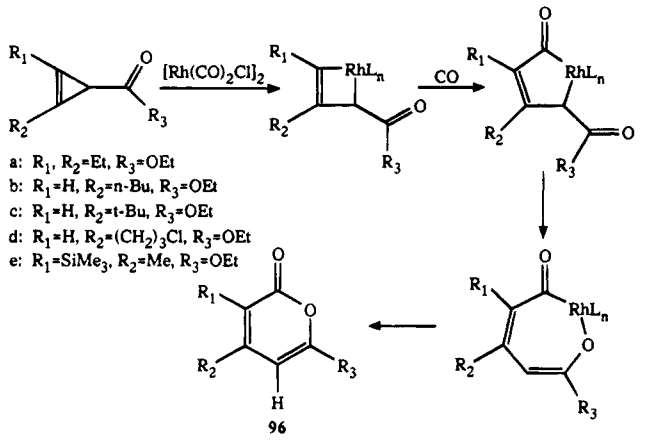


A rhoda(III)cyclobutane intermediate also is suggested for the Rh(I)-catalyzed rearrangement of vinylcyclopropanes (Scheme 29).[226,227] The regiospecificity observed for the β-hydride elimination is attributed to the metallacyclic structures.

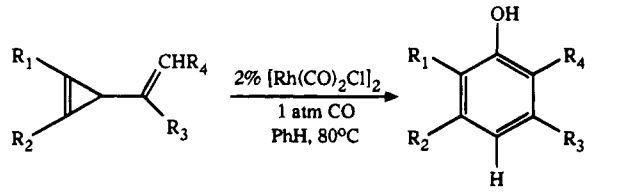
In addition to isomerization reactions, one rhoda(III)cyclobutane intermediate **95** has been proposed as a precursor to four different dimers, formed in 64% yield, in the oligomerization of norbornadiene.[228] Scheme 30 illustrates the proposed pathways suggested to obtain the resulting dimeric products.

In a reaction reminiscent of that shown in eq 94, a rhoda(III)cyclobutane intermediate is invoked in the Rh(I)-catalyzed carbonylation of cyclopropenyl esters and ketones to form α-pyrones (Scheme 31).[229] A variety of substituted organic substrates have been utilized, and in some instances a mixture of α-pyrone

Scheme 31

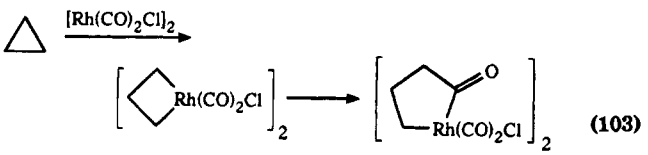


isomers and formation of furan isomers occurs. Scheme 31 shows only those substituent patterns that produce **96** as the major product in greater than 60% yields. The same pathway is suggested for the formation of phenols from vinylcyclopropenes (eq 102).



(102)

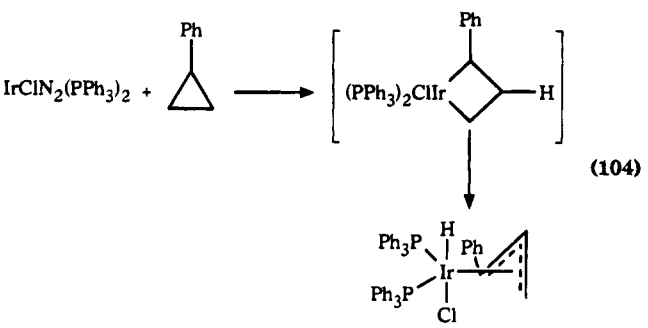
The synthesis of rhoda(III)cyclopentanone dimer also is believed to result from initial rhodium(I) insertion into cyclopropane to form a rhoda(III)-cyclobutane intermediate. Subsequent migratory insertion leads to the observed metallacyclic enolate product (eq 103).[230]



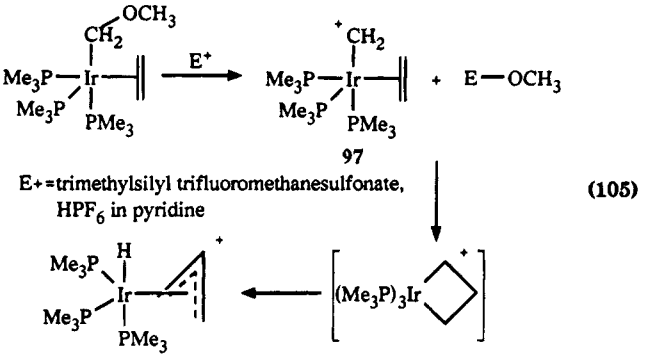
(103)

D. Irida(III)cyclobutane Derivatives as Intermediates

The synthesis of π-allyl iridium hydride complexes has been proposed to proceed via an irida(III)-cyclobutane intermediate. Two examples are shown as eqs 104 and 105. In eq 104, the irida(III)cyclobu-



(104)

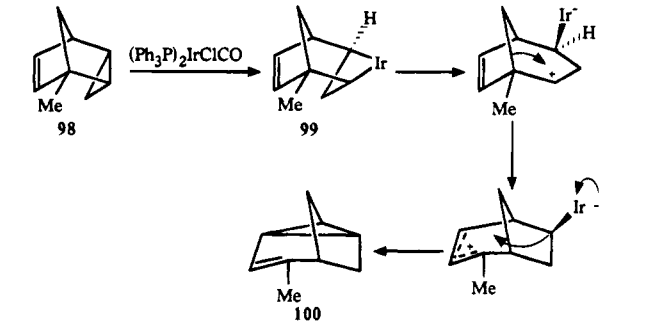


(105)

tane intermediate is formed by insertion of Ir(I) into the 1,2 carbon–carbon bond of phenylcyclopropane.[231,232] The metallacyclic intermediate formed in the reaction shown in eq 105, however, is created by rapid bond formation between the methylene ligand and the ethylene moiety of **97**.[233] In both cases, the irida(III)cyclobutane intermediate subsequently undergoes β-hydride abstraction to form the π-allyl iridium hydride product.

The iridium(I)-catalyzed carbocyclic rearrangement of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **98** to tricyclo-[3.2.1.$0^{2,7}$]oct-3-ene **100** reportedly occurs via the initial formation of an irida(III)cyclobutane intermediate **99**.[234,235] **99** is formed by iridium(I) insertion into the central carbon bond of the tricyclo ring system. The proposed rearrangement pathway for the methyl substituted substrate is outlined in Scheme 32.

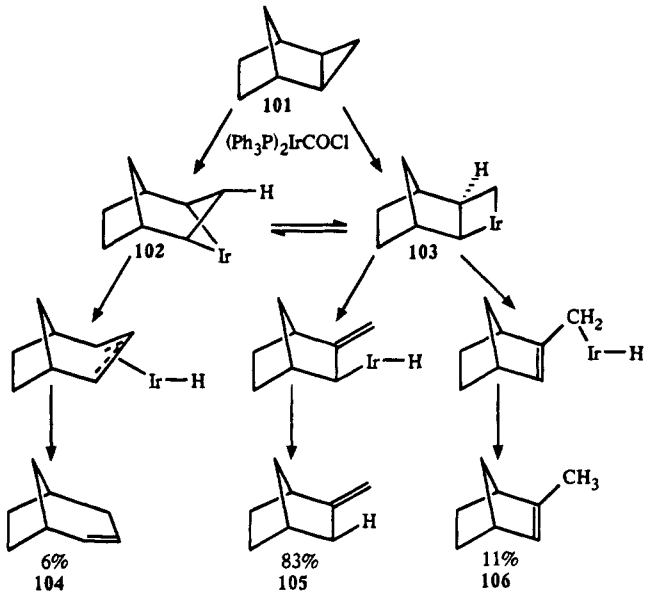
Scheme 32



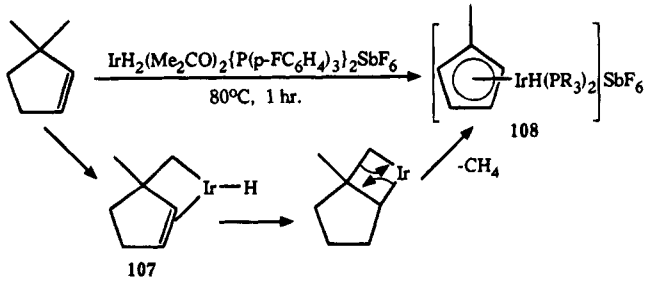
Similarly, two irida(III)cyclobutane intermediates, **102** and **103**, are proposed for the iridium(I)-catalyzed rearrangement of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene and -octane. Scheme 33 demonstrates the rearrangement of **101** to the observed products **104**–**106**.[234] It is possible that the metallacyclic intermediates are formed by initial insertion into two different edges of the cyclopropane moiety or perhaps the iridium inserts into one edge and equilibrates via a Puddephatt-type rearrangement.

The reaction of 3,3-dimethylcyclopentene with an iridium complex to form **108** also invokes an irida-(III)cyclobutane intermediate (Scheme 34).[236] The metallacyclic intermediate is formed by olefin insertion from the iridium hydride complex **107**. A metathesis-like cleavage then occurs to eventually lead to the observed product, **108**.

Scheme 33

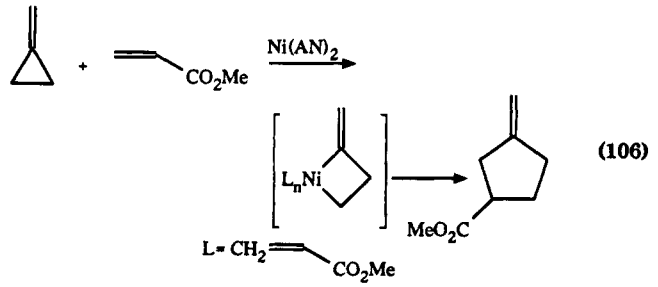


Scheme 34



E. Nickela(II)cyclobutane Derivatives as Intermediates

Nickel(0)-catalyzed cycloaddition reactions often proceed through a nickela(II)cyclobutane intermediate. The $[2\sigma + 2\pi]$ cycloaddition of methylene cyclopropane and methyl acrylate in the presence of bis(acrylonitrile)nickel(0), shown in eq 106, is one example.[237-239] However, a similar reaction utilizing a $Ni(COD)_2$ catalyst led to additional products and prompted investigators to suggest an alternate reaction pathway involving a nickela(II)cyclopentane intermediate.[240]

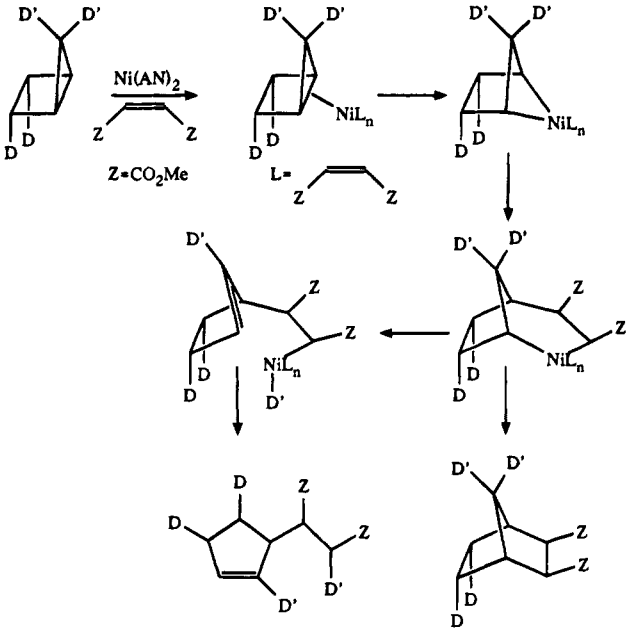


(106)

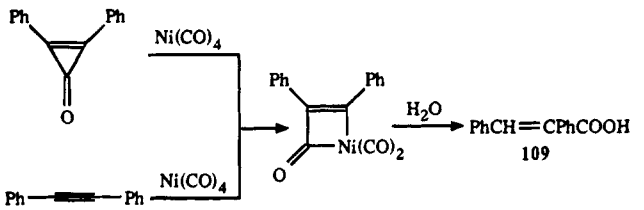
A nickela(II)cyclobutane intermediate also has been reported for the cycloadditions of bicyclo[1.1.0]butane, bicyclo[2.1.0]pentane, and quadricyclane with electron-deficient olefins.[241-243] The general reaction scheme for the deuterium-labeled bicyclo[2.1.0]pentane example is shown in Scheme 35.

Nickela(II)cyclobutenone intermediates are proposed for the reactions shown in Schemes 36 and 37.

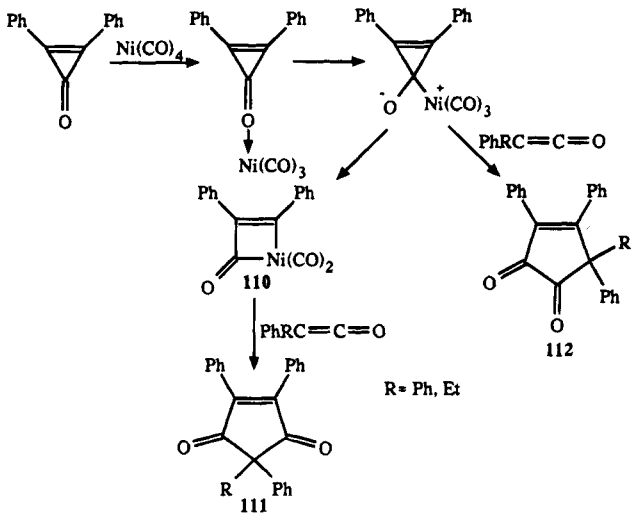
Scheme 35



Scheme 36



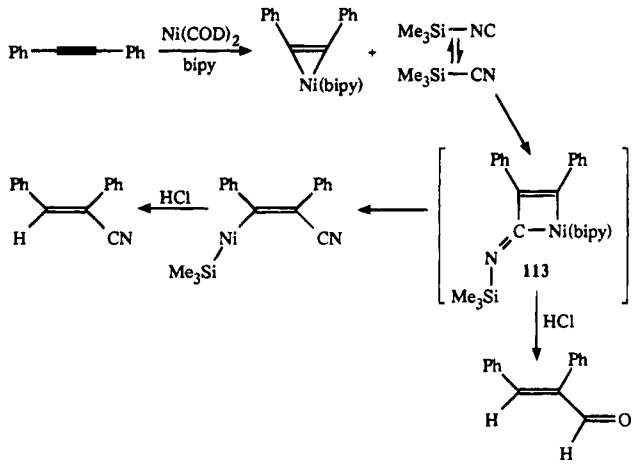
Scheme 37



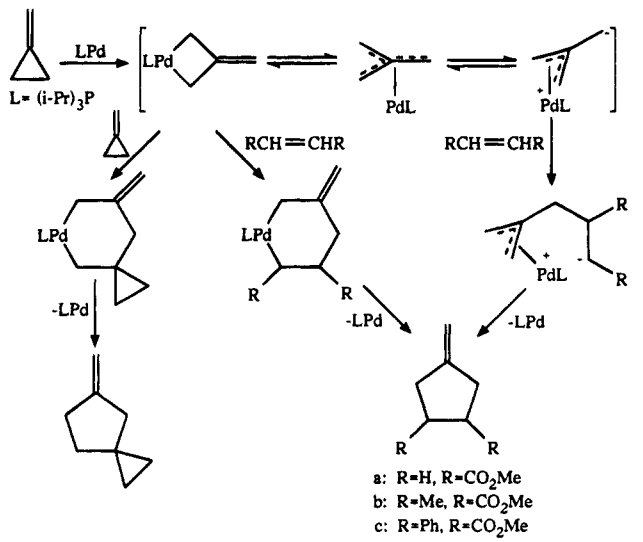
Scheme 36 illustrates the reaction of either diphenylcyclopropenone or diphenylacetylene with tetracarbonylnickel(0) and water to form **109**.[244] In Scheme 37, Ni(0) catalyzes the cycloaddition of diphenylcyclopropenone and ketene to yield **111** and **112**.[57,245] **111** is suggested to form via a metallacyclobutenone intermediate **110** as shown.

Reaction of diphenylacetylene with Ni(0) forms a nickela(II)cyclopropene that when treated with trimethylsilylisocyanide forms products which are indicative of a nickela(II)cyclobutenimine intermediate **113** (Scheme 38).[246]

Scheme 38



Scheme 39

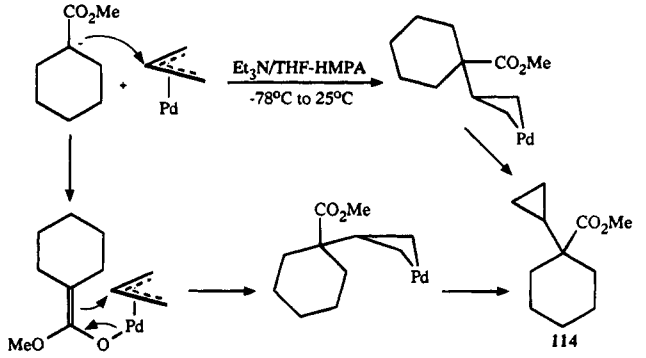


F. Pallada(II)cyclobutane Derivatives as Intermediates

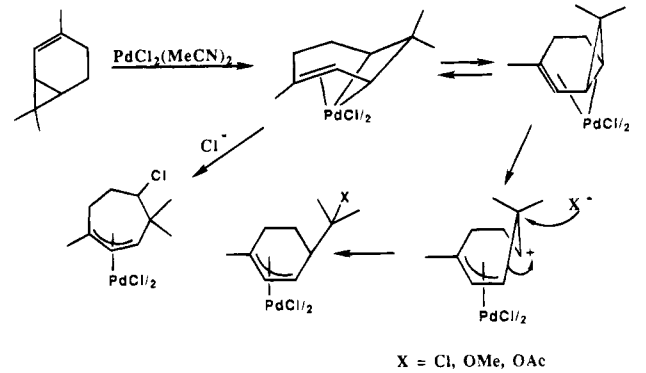
In accordance with the reaction shown in eq 106 of the previous section, the palladium(0)-catalyzed $[2\sigma + 2\pi]$ cycloaddition of methylenecyclopropane and olefins also presumably proceeds through a metallacyclic intermediate. In contrast to nickel, however, palladium(0) apparently cleaves the methylenecyclopropane at the C_2-C_3 bond rather than at the C_1-C_2 bond to form the trimethylenemethane intermediate. An example of this process is illustrated in Scheme 39.[247,248] Further investigations have been performed with various olefins reacting with methylenecyclopropane and 1-methylene-2-vinylcyclopropane and reactions of CO_2 with methylenecyclopropane to form γ-lactones.[249,250] In all cases, initial formation of a pallada(II)cyclobutane intermediate is suggested which subsequently leads to the observed products by various pathways.

A pallada(II)cyclobutane intermediate also is invoked in the cyclopropanation of ester enolates by π-allyl palladium chloride complexes (Scheme 40).[251] In this example, pallada(II)cyclobutane formation occurs either by direct nucleophilic attack on the central carbon of the π-allyl system or by attack at the palladium center followed by transfer to the

Scheme 40



Scheme 41



π-allyl ligand. In either case, subsequent reductive elimination of cyclopropane from the pallada(II)-cyclobutane intermediate leads to the observed product **114**.

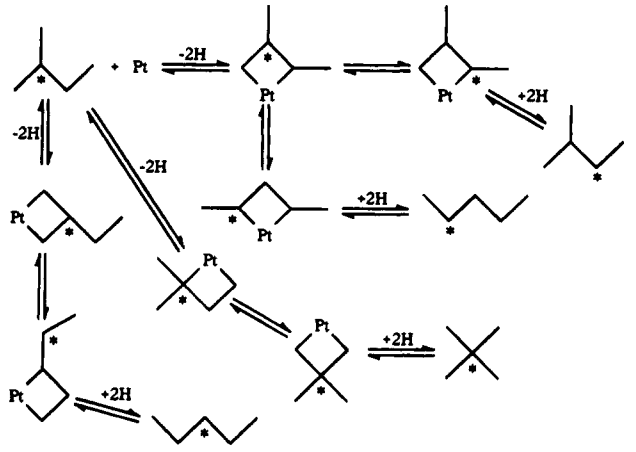
Palladium(II)-induced ring opening of the cyclopropane moiety of a vinylcyclopropane may proceed via a pallada(II)cyclobutane intermediate (Scheme 41).[252]

G. Platina(II)- and -(IV)cyclobutane Derivatives as Intermediates

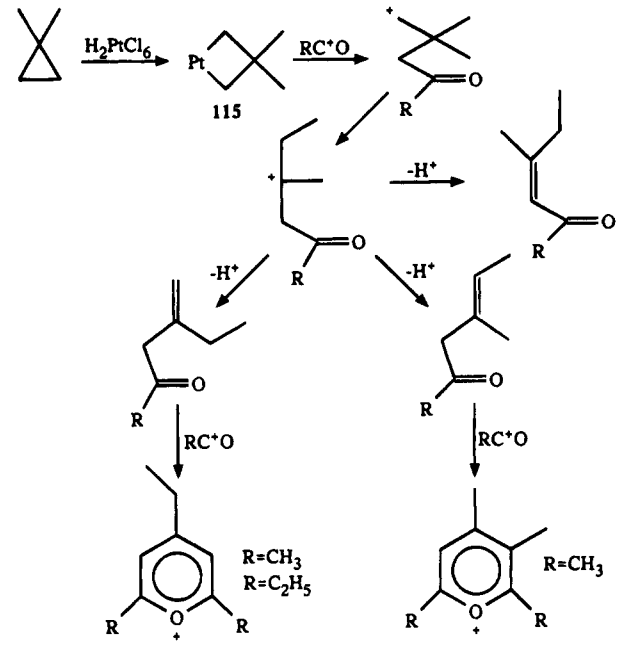
Both platina(II)- and platina(IV)cyclobutanes have been suggested as reaction intermediates. The isomerization of pentanes over platinum metal catalysts invokes a platina(II)cyclobutane intermediate, with possibly two or three platinum atoms interacting, to account for the observed products.[253] A similar mechanism has been developed for this isomerization that supports a single platinum center interacting with pentane and also employs the known intramolecular isomerization observed with platina(IV)cyclobutanes (Scheme 42).[47,73]

The reaction of chloroplatinic acid and methyl-substituted cyclopropanes, in acetic anhydride, failed to yield the expected stable platina(IV)cyclobutane that results from the unsubstituted cyclopropane analogues (Scheme 43). The observed products were instead pyrilium ions which are believed to form via a platina(IV)cyclobutane intermediate **115**.[60] It is suggested that the methyl-substituted platina(IV)-cyclobutane formed **115** is more susceptible to electrophilic attack by the acylium ion than its unsubstituted analogue. Therefore, acylation and subsequent pyrillium ion formation is favored over precipitation of a stable platina(IV)cyclobutane tetramer. Although a C_2-C_3 bond cleavage of cyclopro-

Scheme 42



Scheme 43

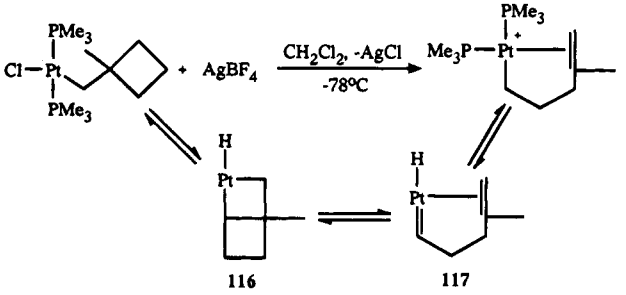


pane to form intermediate **115** is proposed, the possibility that platinum insertion into the C_1-C_2 bond initially occurs followed by isomerization to **115** cannot be excluded. Acylation of the platina(IV)-cyclobutane intermediate and cleavage of the carbon–platinum bond then occurs, followed by methyl migration and proton loss to form the β,γ-unsaturated ketones. Additional acylation of the ketone species then leads to formation of the pyrillium ions.

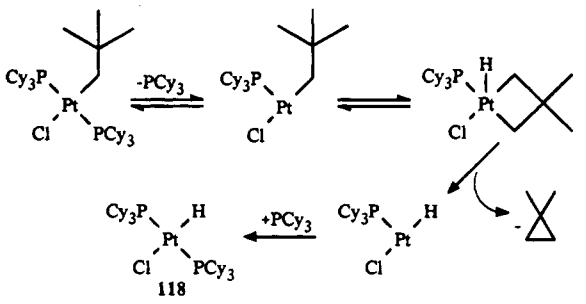
In a study of β-alkyl eliminations, the rearrangement shown in Scheme 44 was proposed en route to the final products.[254] Although it appears to be a β-alkyl elimination, this pathway cannot be distinguished from γ-C–H activation process that forms a platina(IV)cyclobutane intermediate **116** as shown. Although platina(IV)cyclobutanes are normally resistant to ring cleavage, it is suggested that the intermediate **116** may be susceptible to ring cleavage to form **117** due to the strain energy from the cyclobutane moiety.

A γ-C–H activation to form a platina(IV)cyclobutane intermediate is proposed for the thermal decomposition of *trans*-chloroneopentylbis(tricyclopentylphosphine)platinum(II) to 1,1-dimethylcyclopropane

Scheme 44

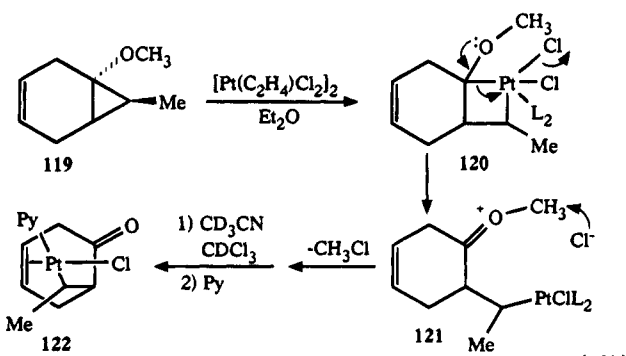


Scheme 45



and the platinum complex **118**.[255] Scheme 45 illustrates the metallacyclic intermediate formation which subsequently reductively eliminates the observed cyclopropane. Addition of ligand to the remaining platinum species creates the observed *trans*-chlorohydridobis(tricyclopentylphosphine)platinum(II) complex **118**.

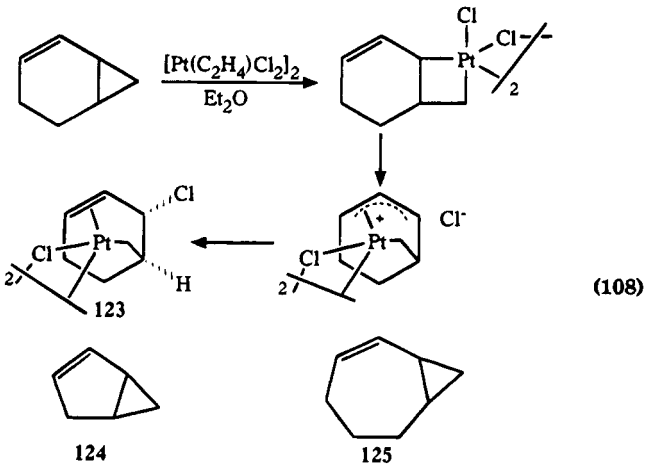
A novel tetrasubstituted platina(IV)cyclobutane intermediate is proposed for the reaction shown in eq 107.[256] Pt(II), in the form of Zeise's dimer, is inserted into the most highly substituted bond of the cyclopropane moiety of **119** to form the tetrasubstituted platina(IV)cyclobutane intermediate **120**. Further reaction leads to the observed platinum(II)–olefin complex **122**.



(107)

Continued investigations of unsaturated bicyclo[x.1.0] ring systems led to the formation of another platinum(II)–olefin complex **123**.[91] Equation 108 illustrates the proposed pathway which proceeds via initial insertion of Pt(II) into the cyclopropane moiety to form the platina(IV)cyclobutane intermediate. The vinylcyclopropane ring systems **124** and **125** form analogous platinum(II)–olefin species. Nucleophiles

other than Cl^- have been used (i.e., ROH, RSH, RCOONa, $CH_2{=}C(-OSiR_3)CH_3$).[81]

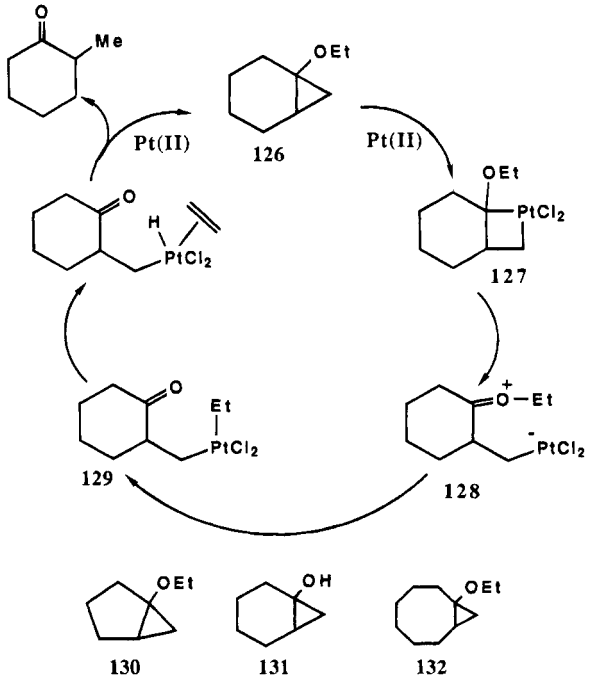


(108)

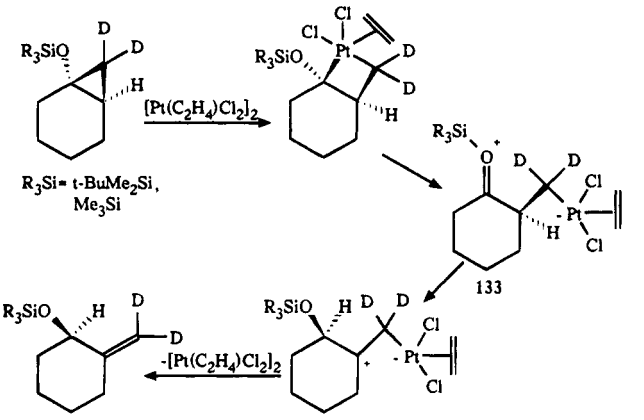
The platinum(II)-catalyzed rearrangement of **126** to form 2-methylcyclohexanone is believed to occur by the catalytic cycle shown in Scheme 46.[91] The platina(IV)cyclobutane intermediate **127** and intermediate **128** are analogous to intermediates **120** and **121** in eq 107. However in the absence of an olefin, the platinum–ethyl moiety is formed, **129**, which upon β-hydrogen abstraction and subsequent reductive elimination forms the observed 2-methylcyclohexanone product. The bicyclic ring systems, **130**–**132**, also catalytically form their respective methyl cycloketones upon addition of Zeise's dimer.

Zeise's dimer is proposed to catalyze the isomerization of siloxycyclopropanes to *exo*-methylene silyl ethers.[67] The suggested reaction pathway for one example is shown in Scheme 47. Again, Pt(II) insertion into the most highly substituted bond of the cyclopropane moiety is proposed to form the platina(IV)cyclobutane intermediate. Subsequent heterolytic cleavage of the platinum–siloxy carbon bond

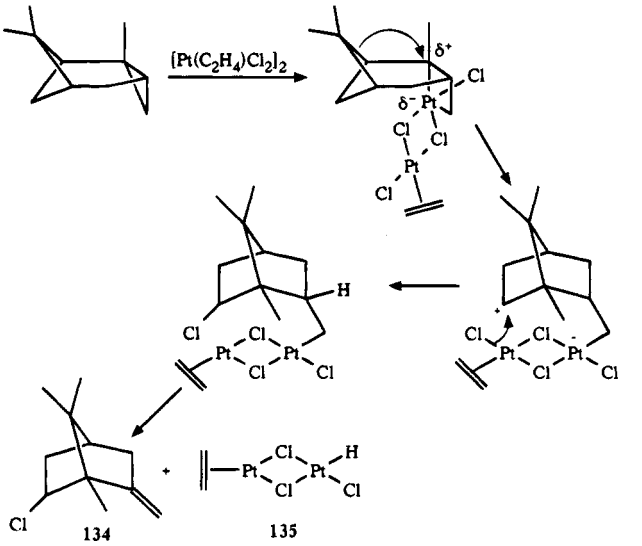
Scheme 46



Scheme 47



Scheme 48



forms the zwitterionic intermediate **133** which proceeds via a 1,2-hydride shift to the observed product. This reaction has been found to be quite general for a variety of 2-alkyl-substituted siloxy cyclopropanes.

When cyclopropanated α-pinene reacts with Zeise's dimer, an exocyclic methylene complex results in concert with that shown above. However, this reaction is not catalytic with Pt(II). Scheme 48 illustrates the proposed pathway for this reaction.[257] Initial formation of a platina(IV)cyclobutane intermediate occurs followed by bridge migration. A chlorine is then believed to be transferred from the Pt(II) to the organic substrate. However, it is not certain whether this is an intramolecular process (as shown) or an intermolecular process. Subsequent β-hydride elimination then leads to the formation of **134** and the Pt(II) complex **135** which further decomposes to HCl, Pt(0), and $PtCl_2$. The trimethylsiloxy analog of α-pinene (i.e., trimethylsiloxy replacing the methyl group on the cyclopropyl portion) follows the pathway Scheme 47 rather than 48. These contrasting results are rationalized on the concept that the siloxy cation is more stable than the methyl cation. The latter is subsequently stabilized by bridge migration (i.e., early vs late transition states).[257]

VI. Summary of Chemistry Section

In section IV, 10 topical reaction types have been discussed and several proposed mechanstic pathways

presented. Not all of the mechanistic sequences have been detailed and/or criticized. This will be left for the individual investigators.

It is interesting to note that platinum(IV) is unique at this time in its ability to rearrange intramolecularly so as to place the metal atom in any one of the cyclopropane bonds. While there are similar rearrangements postulated for platinum(II) and Co(III), they are not corroborated with ample evidence. It appears clear that Fe, Rh, and Ir do not have the ability to rearrange in this manner.

While there are olefin-forming reactions which formally appear to be β-hydride eliminations from metallacyclobutanes, there is a question and an opportunity to determine if this is a cascade initiated by an α-hydride transfer or a transannular hydride or proton abstraction mechanism.

Several metallacyclobutanes are proposed as intermediates in reaction sequences. There are unique opportunities here in that these processes can yield organic transformations that may be catalytic. In addition, with the platinum(IV) systems and their propensity to yield cationic intermediates, it is reasonable to expect that bond insertion/reaction specificity may be achieved.

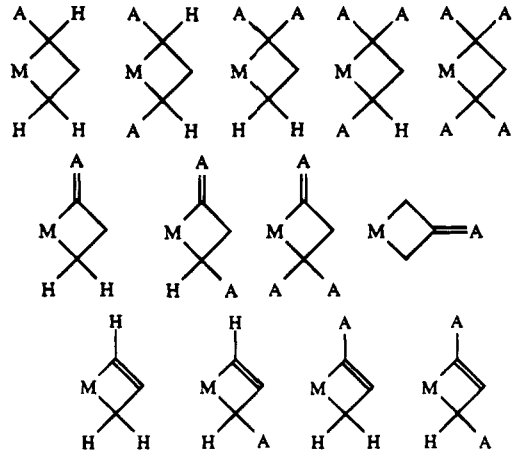
VII. Literature Search

Unique problems are discussed below which arose in searching the computerized literature. CAS Online, a Chemical Abstracts Service available through STN International, was employed for this purpose.[258] Upon accessing the CAS files, a structure search was performed by drawing a metallacyclobutane according to the commands of the CAS Online manual (*Building and Searching Structures on STN*). The structure was very simple, specifying only the metals of the group eight transition metals. It was hoped that by conducting a search of a metallacyclobutane that could have either single or double bonds and any type of substitution that no metallacyclobutane derivative would be excluded from the search.

A range search was conducted on the specified structure from 1984 to the present. Upon viewing the search output, however, it became apparent that the structure search would need to be modified and retrieving the desired literature would not be quite so facile. Included in the retrieval, along with the desired metallacyclobutane derivatives, were metal–η^3-allyl complexes and complexes with a cyclopentadienyl ligand coordinated to the metal. (See structures in Chart 1.) Both of these unexpected complexes are contained in a plethora of publications, making production of a hardcopy of the search output unrealistic.

To circumvent the inclusion of these unwanted structures in our search output, it was necessary to draw structures with specific attributes. For example, by specifying a metallacyclobutane with all single bonds the η^3-allyl species were eliminated. Unfortunately, of course, so were any metallacyclobut*ene* complexes but not the metal–Cp or –Cp* species. To exclude the Cp or Cp* ligands, two substituents, two hydrogens, or a hydrogen and one substituent could be placed at any carbon. These structures did not exclude the η^3-allyl species, however. Examples of the structures used in the search are shown in Chart 1.

Chart 1



It was not possible to exclude both unwanted species while still obtaining all the desired metallacyclobutane derivatives by doing a single structure search. However, by searching 15–20 specific structures a successful search of the literature for metallacyclobutane derivatives of the group eight transition metals was achieved.

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