ELSEVIER

Coordination Chemistry Reviews
193–195 (1999) 207–281

COORDINATION
CHEMISTRY
REVIEWS

www.elsevier.com/locate/ccr

The chemistry of group 10 metalacycles

Juan Cámpora *, Pilar Palma, Ernesto Carmona

Departamento de Química Inorgánica-Instituto de Investigaciones Químicas,
Universidad de Sevilla-Consejo Superior de Investigaciones Científicas, C/ Americo Vespucio s/n,
Isla de la Cartuja, 41092 Sevilla, Spain

Received 7 December 1998

Contents

---

* Corresponding author. Tel.: +34-95-4489553; fax: +34-95-4460565.

PII: S0010-8545(99)00047-8

Abstract

Metalacycles of Nickel, Palladium and Platinum in which the metal binds two carbon atoms form a rapidly growing class of compounds that find diverse applications in organic synthesis both in stoichiometric and catalytic reactions. We address herein the synthetic approaches used in the preparation of these complexes, and their chemical reactivity, with emphasis in processes such as the insertion of small unsaturated molecules into the metal–carbon bonds, which lead to the formation of organic products.

Keywords: Metalacycles; Nickel; Palladium; Platinum; Catalysis

---

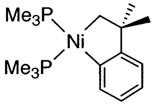
Nomenclature

BAr_4	tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
bipy	2,2′-bipyridine
bipym	2,2′-bipyrimidine
cod	1,5-cyclooctadiene
dba	dibenzylideneacetone
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dmad	dimethyl acetylenedicarboxylate
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenilphosphino)ferrocene
dppm	1,2-bis(diphenylphosphino)methane
nbd	norbornadiene
OMs	mesylate (methanesulphonate)
OTf	triflate (trifluoromethanesulphonate)
phen	1,10-phenanthroline
pmedta	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine
py	pyridine
THF	tetrahydrofuran
THT	tetrahydrothiophene
teeda	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
tmda	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
Tp	tris(pyrazolyl)borate
Tp*	tris(2,3-dimethylpyrazolyl)borate

1. Aims and Scope

A metalacycle can be defined [1] as 'a carbocyclic system with one or more atoms replaced by a transition metal'. This definition limits metalacyclic complexes to those in which the metal is bound to two carbon atoms, and therefore excludes simple complexes containing chelating phosphines, cyclometalated compounds and any other cyclic complex in which the metal is bound to a heteroatom. Even with such limitations, the chemistry of metalacycles has experienced a notable development during the last years, in part due to their involvement in different catalytic processes and their applications in organic synthesis, some of which can be found in the currently available reviews on the subject [1–10].

Our interest in metalacycle chemistry was triggered by the synthesis in our laboratories of the nickel metalacycle **1** in 1986 [11,12]. Although it might be anticipated that metalacycles should display similar properties to open-chain dialkyl transition metal complexes, compound **1** exhibits a high reactivity, with chemical properties rather different from other Ni(II) alkyl or aryl complexes, which can be applied to its transformation in a wide variety of organic compounds (see Refs. [13,14] for two brief accounts). Since then, the metalacyclic chemistry of Ni and Pd has been a current research topic in our laboratories, and thus we feel that a general account of the field, including the related Pt compounds, would be worthwhile. The limitation of this review to the group 10 metals is imposed not only by reasons of immediate interest, but also by the wide amount of information available for any other group in the transition series. In order to keep the matter within a reasonable limits, we have also excluded from this review some other compounds that would also fit the metalacycle definition, such as ylides, chelating carbenes, and trimethylenemethane complexes and the related oxa- and aza- derivatives, which can be considered closer in structure and properties to η^3-allyl complexes. However, we have included some metalacycles that contain a heteroatom within the cycle, and we have also described some chemistry of other not strictly metalacyclic complexes.



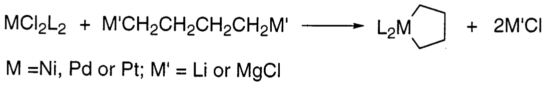
1

2. Synthesis of metalacycles

2.1. Transmetalation reactions

One of the classical methods for the preparation of open-chain metal alkyls, the transmetalation reaction, has often been applied to the synthesis of metalacycles, giving access to compounds that cannot be prepared by other procedures. Although in principle any ring size can be obtained, five-membered rings are, by far, the most frequently synthesized. The preparation of metalacycles with other ring sizes will be discussed at the end of this section.

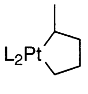
Some early metalacycloalkane derivatives of group 10 elements were the metalacyclopentanes, shown in Eq. (2.1), obtained from α,ω-dilithium or dimagnesium derivatives.



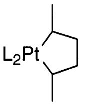
(2.1)

Platina- and nickelacyclopentanes were discussed almost simultaneously by Whitesides [15,16] and Grubbs [17–19], respectively, in the seventies, in a series of classical mechanistic studies on the decomposition of platinum and nickel metalacycles. The preparation of platinacyclopentane compounds containing the labile cyclooctadiene ligand provided ready access to many other derivatives by simple ligand exchange reactions [15,16]. Analogous palladacyclopentanes containing PPh_3, chelating diphosphines (dppe, dcpe) or nitrogen donors (tmda, bipy) were later prepared by Diversi et al. by treatment of the corresponding palladium dihalides with 1,4-dilithiobutane [20–22].

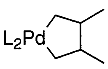
Metalacyclopentanes of Pd [22] and Pt [16,23] containing methyl substituents at the α (**2**, **3**) or β (**4**, **5**) positions of the metalacycle were also made from the corresponding di-Grignard or dilithium reagents. Other five-membered metalacycles obtained by transmetalation reactions include some benzo[c]metalacyclopentenes (*o*-xylylene complexes), metalacyclopentadienes and dibenzometalacyclopentadienes. The first class of compounds is accessible from the di-Grignard reagent **6** (Eq. (2.2)), used by Lappert [24] for the synthesis of metalacyclic complexes of different elements, including platinum, **7**, [25]. More recently, a similar palladium xylylene complex has also been synthesized from the α,α-xylyl di-Grignard reagent by the authors of this review (Eq. (2.3)) [26].



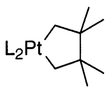
2



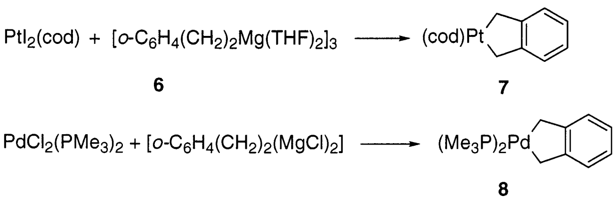
3



4



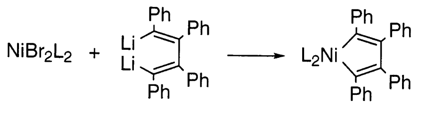
5



(2.2,2.3)

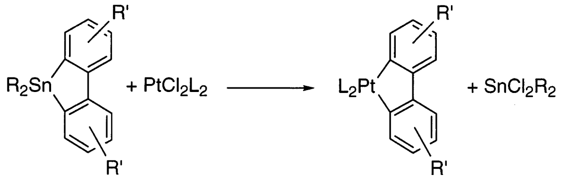
While palladium and platinum metalacyclopentadiene complexes are known to be readily formed by alkyne coupling reactions (see Section 3.3), mononuclear nickel metalacycles of this type are restricted to the tetraphenyl derivatives of type

9, obtained independently by Hoberg [27] and Eisch [28,29] (Eq. (2.4)). Interestingly, the reaction of $NiBr_2(PEt_3)_2$ with one equivalent of 1,2-dilithio-1,2-diphenyl-1,3-butadiene,**10**, gives rise mainly to the cyclooctatetraene complex **11**. The use of less than the stoichiometric amount of **10** leads to the binuclear complex **12**, suggesting that the formation of **11** might involve the dimetalacycle **13** (Scheme 2.1) [30].



L_2 = dppe, $(PEt_3)_2$ **9** (2.4)

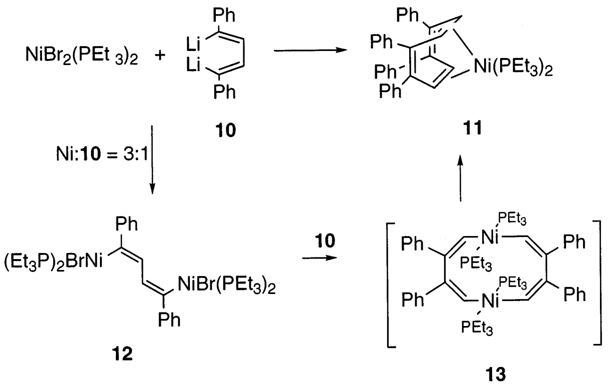
Attempts to use this synthetic methodology to obtain dibenzometalacyclopentadiene complexes of Pt have met only with limited success [31]. More satisfactory results were achieved by Vicente [32], using the stannole reagent **14** (Eq. (2.5), R = *n*-Pr, R′ = H). This method, later extended by Brune [33], has allowed the synthesis of substituted dibenzoplatinacyclopentadienes in 30–60% yield (Eq. (2.5)). The olefin ligands used in this synthesis can be readily replaced by other donors such as bipy, bipym or PPh_3 [32–35].



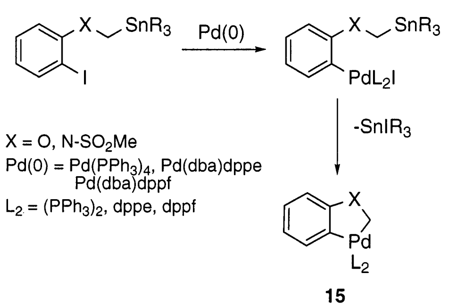
14

L = cod, nbd; R = Pr, Bu; R′ = CF_3, MeO, *t*-Bu (substitution pattern 3,3′ or 4,4′) (2.5)

Scheme 2.2 shows an elegant method devised by Echevarren and co-workers [36–38] for the synthesis of the heteroatom-substituted palladacycles **15**. This



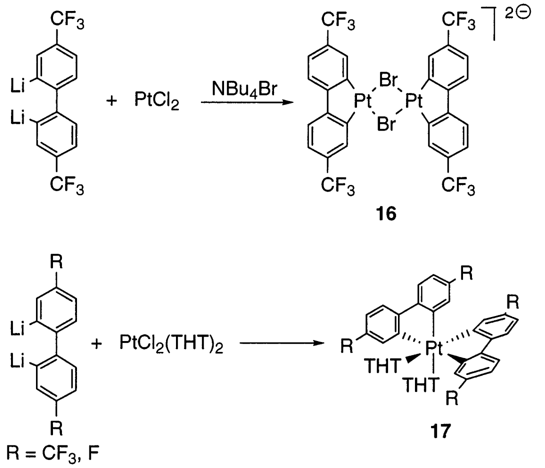
Scheme 2.1.



Scheme 2.2.

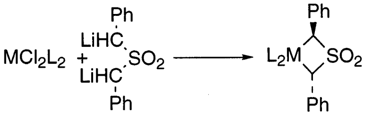
oxidative addition-transmetalation reaction illustrates the mechanism of the widely used Stille coupling reaction. The final reductive elimination that closes the catalytic cycle in the latter does not take place in the case of the intramolecular transmetalation, since it would involve the formation of strained four membered heterocycles.

In the course of studies aimed at the synthesis of nickelacyclopentanes using 1,4-dilithiobutane, Grubbs et al. noted that the use of an excess of the alkylating agent leads to the formation of a brown *ate*-type complex of composition $Ni(CH_2)_4(L_2)\cdot Li_2(CH_2)_4(Et_2O)_4$ [19]. This reaction has been recently used by Fröhlich for the synthesis of anionic metalabicyclic derivatives of Ni [39,40], Pd [41] and Pt [39,42–44]. That of the nickel derivatives requires the use of halide-free $1,4\text{-}Li_2(CH_2)_4$ and nickelocene or the *ate* complex $K[Ni(NPh_2)_3]$ [39]. Interestingly, the reaction of $PtCl_2(cod)$ with the dilithium reagent $LiCH_2SiMe_2SiMe_2CH_2Li$ failed to give the homoleptic metalacyclic platinate, and produced instead the neutral metalacycle $\overline{Pt(CH_2SiMe_2SiMe_2C}H_2)(cod)$ [43]. Brune has also attempted the synthesis of related bis-metalacycle platinate complexes by reacting $PtCl_2$ with a ten-fold excess of 2,2′-dilithiobiphenyl, but the reaction led, after aqueous workup, to the binuclear metalacyclic complex **16** [45] (Eq. (2.6)). Surprisingly, a similar reaction using $PtCl_2(THT)_2$ afforded the Pt(IV) metalabicycle **17** (Eq. (2.7)) [46,47].



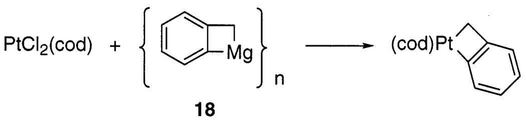
(2.6,2.7)

The transmetalation procedure has also been used for the synthesis of other than five-membered metalacyclic units [15,16,48]. $Ni(CH_2)_5(PPh_3)_2$ is an example of a six-membered ring [48]. Whilst the synthesis of four-member metalacycles by transmetalation appears to be unusual, a platinacyclobutane complex has been obtained by treatment of $PtI_2(cod)$ with $BrMgCH_2CMe_2CH_2MgBr$ [49]. Eqs. (2.8) and (2.9) show other related examples [50–53]. However the interaction of $NiCl_2(bipy)$ with the magnesium reagent **18**, developed by Bickelhaupt [53a] provided the 6,7-dihydro-5H-dibenzo[c,e]nickelepine **20** along with Ni(0) [54], in a process suggested to involve the bimetalacyclic complex **19** (Scheme 2.3) as an active intermediate.



M = Ni; L = PMe_3 or dppe
M = Pd, L = PPh_3, PMe_3 or PEt_3
M = Pt, L = $AsPh_3$, PPh_3 or SEt_2

(2.8)

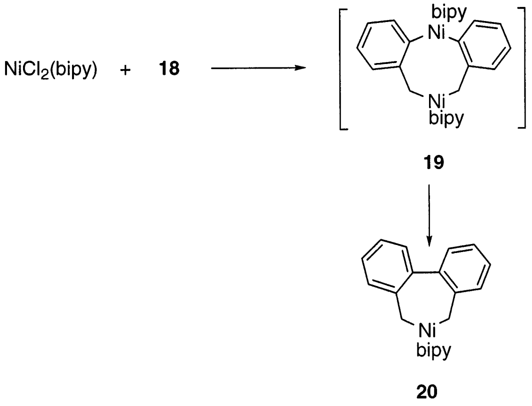


18

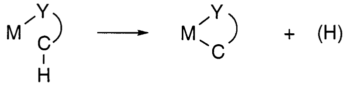
(2.9)

2.2. Cyclometalation

The intramolecular C–H activation reaction, or cyclometalation reaction, as defined by Eq. (2.10), provides access to a wide range of metalacyclic derivatives of



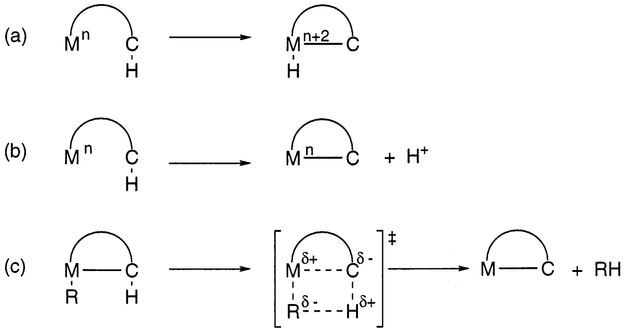
Scheme 2.3.



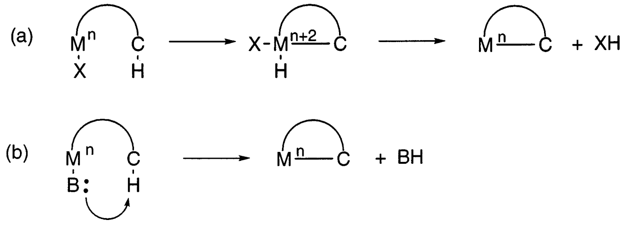
(2.10)

the transition metals [55–58]. For most of the compounds prepared by this method Y is a two electron donor heteroatom, consequently they will not be covered in this review. However, the cyclometalation of alkyl complexes ($Y = CR_2$–) provides a route to metalacycloalkanes and other related species.

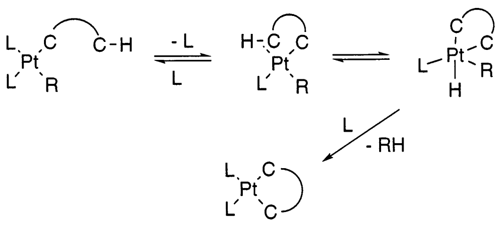
It is well established [58] that from a mechanistic point of view the cyclometalation reaction can be classified into the types shown in Scheme 2.4, namely, oxidative addition (a), electrophilic substitution (b), and multicentered or concerted pathway (c). While there is very little experimental evidence in support of a (c)-type mechanism in the Ni group (see for example Ref. [12]) considerable effort has been devoted to distinguish between paths (a) and (b). This distinction would appear to be deceptively straightforward from Scheme 2.4, but for M(II), d^8 systems both pathways actually afford the same products. Thus, since hydrides of the type shown in path (a) readily experience reductive elimination processes, and on the other hand, path (b) needs the assistance of a base, that may enter the coordination sphere of the metal, the overall picture of mechanisms (a) and (b) results extremely similar (Scheme 2.5).



Scheme 2.4.

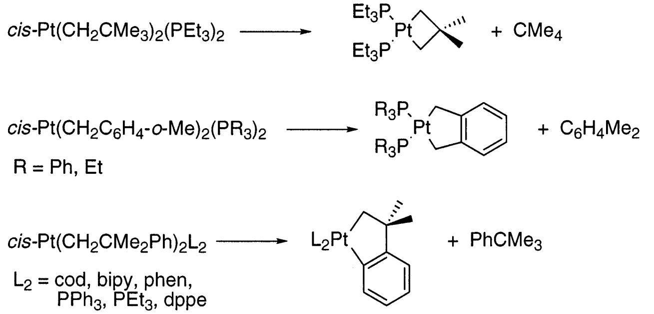


Scheme 2.5.



Scheme 2.6.

The thermolysis of different platinum dialkyl complexes that lack β-hydrogen atoms lead to the formation of metalacycles along with the corresponding hydrocarbons (Eqs. (2.11) [59–62]; (2.12) [63,64] and (2.13) [65,66]).

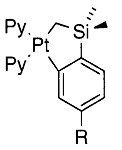


(2.11,2.12,2.13)

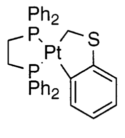
Whitesides [61,62] has subjected the reaction depicted by Eq. (2.11) to detailed mechanistic studies, and Young [66] has carried out a similar investigation on the cyclometalation of platinum bis(neophyl) complexes (Eq. (2.13)). These reactions follow first order kinetics, and as demonstrated by isotopic labeling experiments, are strictly intramolecular. The experimental evidence accumulated is in full agreement with the mechanism presented in Scheme 2.6. In accord with this mechanism, the thermal cyclometalation of bis(neophyl) platinum complexes containing phosphine ligands of larger size than PEt_3 (PPh_3, $P(i\text{-}Pr)_2$ or PCy_3) takes place readily even at room temperature [66].

Measurement of the thermolysis rate of the complexes containing deuterated alkyl (neopentyl or neophyl) ligands showed primary isotopic effects ($k^H/k^D > 3$), indicating that either C–H scission (oxidative addition) or formation (reductive elimination) takes place at the rate limiting step. In the case of the bis(neophyl)platinum complexes that contain chelating ligands such as bipiridine or bipirymidine, a smaller isotopic effect was found ($k^H/k^D = 1.26$), in accord with a control of the reaction by the opening of the bipy or bipym chelate. However for the extremely rigid phenantroline-type ligands, primary isotopic effects were again detected. This, and the observation of substantially larger activation energies than in the bipy or bipym systems indicate that opening of the phenantroline chelate may not be a prerequisite for the cyclometalation process [66]. At variance with the intramolecular pathway described in Scheme 2.6, the photochemical cyclometalation of $Pt(CH_2CMe_2Ph)_2(dppe)$ takes place through a radical pathway involving Pt–C homolysis and H abstraction by the resulting neophyl radical [67].

The thermolysis of platinum bis(2,2-dimethyl)-alkyl complexes containing alkyl chains of different lengths seem to proceed by the mechanism of Scheme 2.6 and gives rise to mixtures of metalacycles with different ring size [61,62]. From isotopic labeling experiments it was concluded that: (a) the ring strain increases in the expected order 5-member > 6-member > 4-member, and (b) the strain energy difference between platinacyclobutanes and platinacyclopentanes (ca. 5 kcal mol^{-1}) is considerably smaller than that between cyclobutanes and cyclopentanes. Refs. [68,69] describe other thermally induced cyclometalation of platinum dialkyl, leading to the metalacycles **21** and **22**.



21

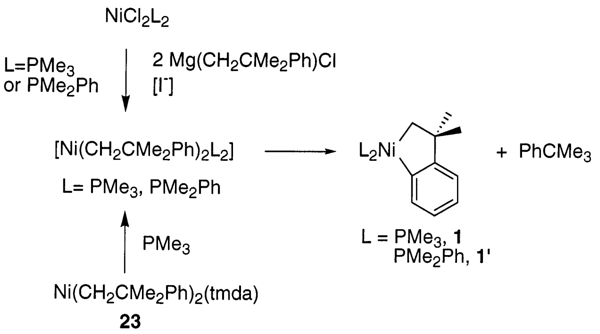


22

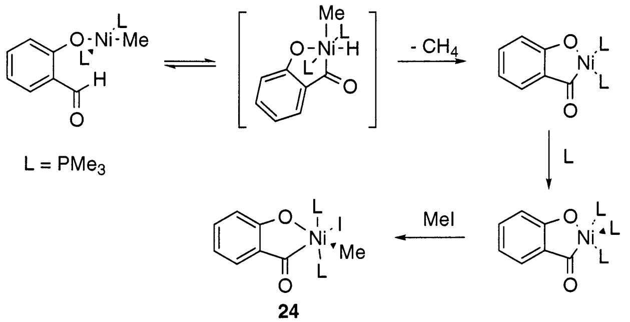
The thermal cyclometalation of dialkyl derivatives of Ni and Pd has also been accomplished. Miyashita [70] reported that the nickel and palladium bis(neopentyl) complexes $Ni(CH_2CMe_3)_2L_2$ ($L = PPh_3$ or L_2 = dppe) and $Pd(CH_2CMe_3)_2(PPh_3)_2$ experience this process to afford the corresponding nickela- and palladacyclobutanes. The labile nickel bis(neopentyl) derivatives decompose below − 20°C, while the Pd analogs had to be heated at 60°C for 1 h. For palladium, competitive reductive elimination from $PdR_2(PPh_3)_2$ also takes place at this temperature, giving ca. 40% of 2,2,5,5-tetramethylhexane.

Benzo[b]nickelacyclopentene complexes of type **1** can be obtained by alkylation of $NiCl_2L_2$ ($L = PMe_3$ or PMe_2Ph) with neophylmagnesium chloride in the presence of catalytic amounts of iodide (Scheme 2.7) [11,12,71]. Dialkylation takes place under these conditions generating a thermally unstable bis(neophyl)nickel intermediate which at room temperature experiences a cyclometalation reaction (Scheme 2.7).

In agreement with this proposal, displacement of the tmeda ligand from the isolable complex **23** by PMe_3 immediately produces **1**. No mechanistic studies were



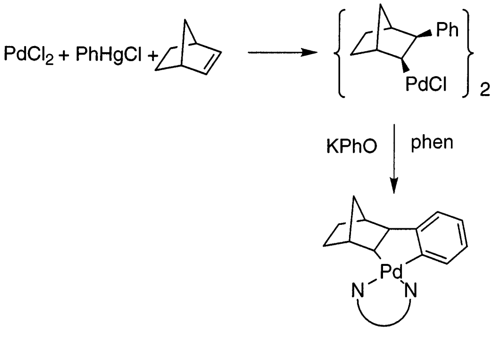
Scheme 2.7.



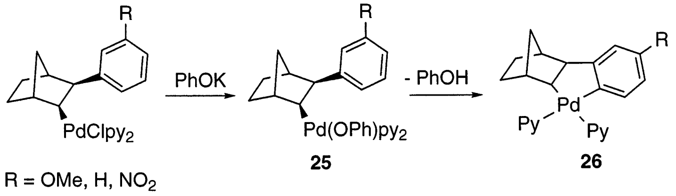
Scheme 2.8.

carried out but the formation of a Ni(IV) hydride intermediate was considered unlikely at that time. It should be noted, however, that a Ni(IV)–H intermediate species (Scheme 2.8) has been proposed recently [72] in a cyclometalation reaction that leads to the structurally characterized Ni(IV) alkyl(acyl) complex **24** [73].

The electrophilic cyclometalation of alkyl(aryl) ligands (mechanism b, Scheme 2.4) is frequently invoked in palladium-catalyzed cyclization reactions (see Section 4), and therefore several research groups have pursued the isolation of stable palladacarbocycles. The formation of these compounds involve the treatment of haloalkyl palladium complexes with bases, a method used in the well-known cyclopalladation reaction [55–58]. Catellani and Chiusoli [7,74–76] have described the formation of palladium complexes by insertion of norbornene into a palladium-aryl bond, using KPhO as a base and phenantroline or PPh_3 as stabilizing ligands (Scheme 2.9). This methodology is very versatile and gives access to metalacycles containing different substituents on the aromatic ring. As expected for a electrophilic substitution process (mechanism (b), Scheme 2.4) measurements of the half-life for the conversion of the corresponding alkyl-phenolate intermediate complexes **25** into metalacycles **26** (Scheme 2.10) showed that the reaction is accelerated by electron donor substituents on the aromatic ring (i.e. the cyclometalation rate decreases in the order MeO > H > NO_2) [76].

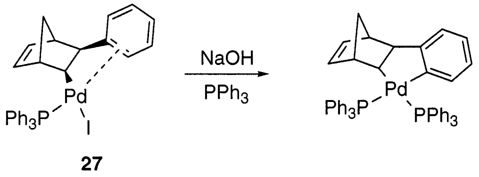


Scheme 2.9.



Scheme 2.10.

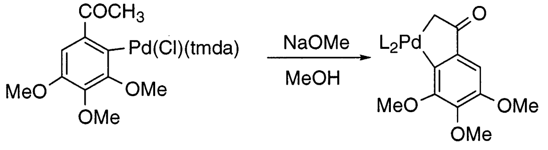
It has been proposed that the activation of aromatic C–H bonds by transition metal compounds requires the previous coordination of the aromatic hydrocarbon to the metal center [77,78]. Cheng has shown that the π-arene complex **27** can be readily cyclometalated by NaOH, suggesting the intermediacy of such species in the cyclometalation process (Eq. (2.14) [79]).



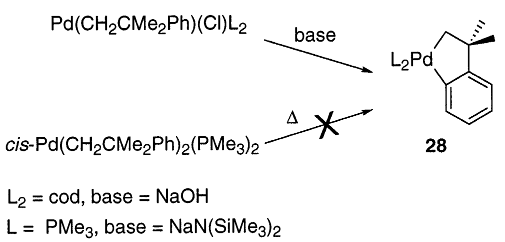
(2.14)

Very recently, our research group has reported the base induced cyclometalation of neophylpalladium complexes (Scheme 2.11) [80,81]. This result is specially noteworthy since, in contrast with the Ni and Pt analogs, $Pd(CH_2CMe_2Ph)_2(PMe_3)_2$ fails to undergo cyclometalation. As discussed in a later section, protonation of the metalacycle **28** ($L = PMe_3$) has provided additional insight into the mechanism of the cyclometalation reaction.

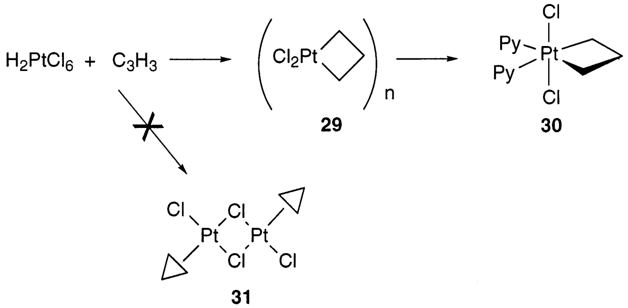
A final example which is worth noting before closing this section is the recent isolation by Vicente and co-workers of the unusual pallada-3-cyclopentenone compound shown in Eq. (2.15) [82].



(2.15)



Scheme 2.11.



Scheme 2.12.

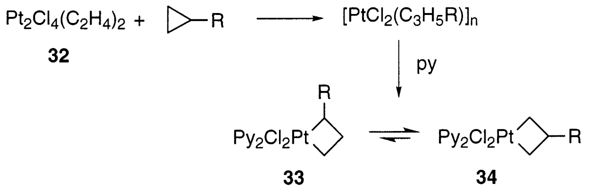
2.3. *Oxidative addition of C–C carbon bonds*

Carbocyclic compounds can oxidatively add to transition metal centers to form metalacycles. The reaction of cyclopropane with hexachloroplatinic acid, reported by Tipper in 1955, gave rise to the first metalacycle of the Ni group, a polymeric platina(IV)cyclobutane **29**, of composition $[PtCl_2(C_3H_6)]_n$ (Scheme 2.12) [83]. This compound reacts with pyridine with formation of the soluble adduct **30.** At that time a dimeric structure analogous to Zeise's dimer **31**, containing an edge-bound, intact cyclopropane ring was proposed to reflect the analogy between cyclopropane and ethylene suggested by Walsh 6 years earlier [84].

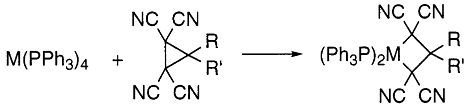
Since the preparation and structural characterization [85–88] of the first platinacyclobutane, this field has expanded steadily and a large number of complexes of this class have been prepared. The metalacyclobutane chemistry of platinum and palladium has been reviewed [6,89] and a recent article by Jennings covers the field up to 1994 [5]. Therefore, only salient aspects of the oxidative addition of cyclobutanes will be considered here.

Both mono- and dialkylated cyclopropane derivatives react with Zeise's dimer, **32**, giving rise to substituted polymeric platinacyclobutanes, which, in turn, can be converted into soluble, mononuclear species by reaction with nitrogen donor ligands, such as pyridine. Although 2-substituted metalacycles **34** are usually obtained from monoalkylated cyclopropanes [5], a mixture of the 1- and 2- isomers may form from arylcyclopropanes [5,90], due to the so-called Puddephatt rearrangement (Scheme 2.13), (see Section 3.2). The Pt(II) center acts as an electrophile in this process, and therefore electron withdrawing substituents (CO_2R, CN or COR) deactivate the cyclopropane ring for this reaction [91]. The electrophilic character of Pd(II) suggests that oxidative addition of alkylcyclopropanes initially gives the 1-substituted product **33**, which subsequently rearranges to the more stable **34** [5].

At variance with the electrophilic behavior of Pt(II), compounds of Pt(0) and Pd(0) react with electron-poor cyclopropane derivatives such as 1,2,2,2-tetracyanocyclopropane (Eq. (2.16)) [89,92–96].



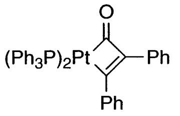
Scheme 2.13.



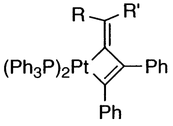
(2.16)

The reaction of cyclopropanes with Ni(0) is at the moment limited to that of cyclopropane itself with nickel atoms to give the unligated metalacycle $Ni(CH_2)_4$, which was detected in an argon matrix [97].

Cyclopropene derivatives, having a higher degree of ring strain than cyclopropanes, react with zerovalent complexes of the Ni group to give metalacyclobutene products. Chronologically, the first reactions of this type were those of cyclopropenone [98] and methylenecyclopropene derivatives [99,100] with Pt(0) complexes which give the platinacyclobutenes **35** and **36**.

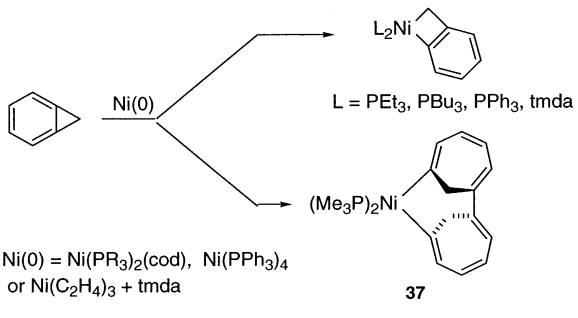


35

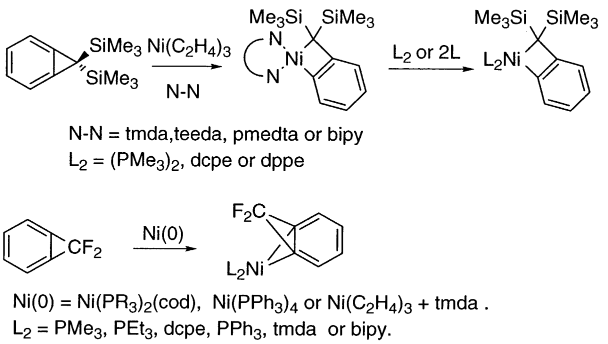


36

Wilke has explored the reactivity of cyclopropabenzenes with Ni(0) and Pd(0). Benzocyclobutane derivatives [101] are in general formed (Scheme 2.14) but with the small PMe_3 ligand, an oxidative cycloaddition reaction, as opposed to a C–C oxidative addition of the cyclopropabenzene is observed and yields the metalacycle **37** [102]. Vollhardt has shown that the highly strained hydrocarbon 3,4-dihydro-1*H*-cyclobuta[a]cyclopropa[d]benzene reacts in a similar way [103] (see next sec-



Scheme 2.14.



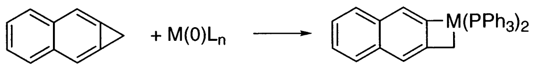
N-N = tmda,teeda, pmedta or bipy
L_2 = $(PMe_3)_2$, dcpe or dppe

Ni(0) = $Ni(PR_3)_2(cod)$, $Ni(PPh_3)_4$ or $Ni(C_2H_4)_3$ + tmda .
L_2 = PMe_3, PEt_3, dcpe, PPh_3, tmda or bipy.

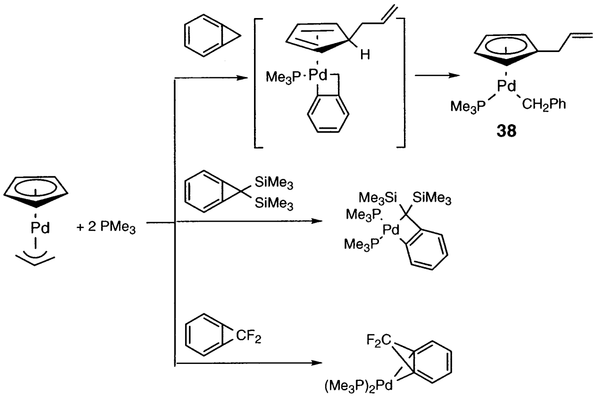
Scheme 2.15.

tion). Substituted cyclopropabenzenes also react with Ni(0) complexes. While 7,7-bis(trimethylsilyl)cyclopropabenzene behaves similarly to cyclopropabenzene itself, affording bis(trimethylsilyl)benzocyclobutanes [104], 7,7-difluorocyclopropabenzene gives a (formally) Ni(0) derivative with propellane structure [105]. Thus, subtle structural changes in the organic substrate or within the ligand system may have a dramatic influence in the reactions of strained unsaturated carbocycles with Ni(0), directing the reaction path towards C–C cleavage or oxidative cycloaddition. As shown in Scheme 2.15 the situation is very similar for Pd(0) although in this case cyclopropabenzene gives the benzyl derivative **38** (Scheme 2.16), through the intermediacy of a reactive palladacyclobutane [106].

Stang has reported that cyclopropa[b]naphthalene reacts with Pd(0), Pt(0) and Rh(I) with oxidative C–C cleavage and formation of the corresponding metalacycles (Eq. (2.17)) [107].

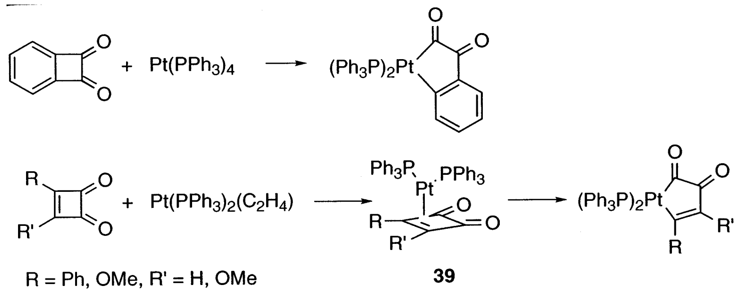


M = Pd, Pt.
$M(0)L_n$ = $Pd(PPh_3)_4$ or $Pt(PPh_3)_2(C_2H_4)$ (2.17)

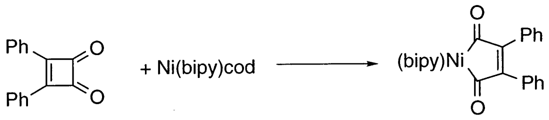


Scheme 2.16.

The C–C bond cleavage of carbocyclic rings larger than cyclopropane or cyclopropene is less common, although it is known that cyclobutene derivatives can also undergo this reaction. Cyclobutenediones react with Pt(0) and Ni(0) complexes giving metalacyclobutenes, but there is a striking difference in the regioselectivity of the reaction. The reaction of $Pt(PPh_3)_4$ with 1,2-benzocyclobutadienequinone [108,109] or substituted cyclobutenediones [110] gives 1,2-platinacyclopentenediones (Eqs. (2.18) and (2.19)). In the latter process, a π-intermediate, **39**, has been detected [111]. Nickel(0) complexes also react with diphenylcyclobutenedione, but the CO–CO bond is cleaved in this case, giving rise to a 1,4-nickelacyclopentene-dione (Eq. (2.20)). As in the above Pt system, an intermediate π-complex can also be detected here [112,113].

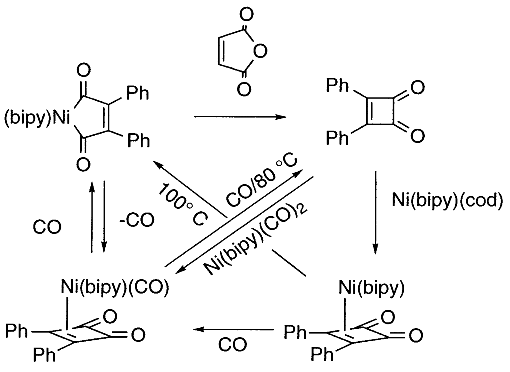


(2.18,2.19)



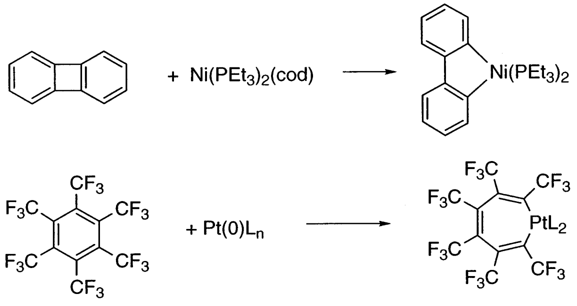
(2.20)

In the next section it will be shown that the same product can be reached by a completely different route that involves Ni(bipy)(cod), diphenyl acetylene and carbon monoxide [112,114]. Rather interestingly, the oxidative addition of the cyclic dione is reversible, and reductive elimination can be induced by reaction with maleic anhydride or carbon monoxide (Scheme 2.17).



Scheme 2.17.

Although benzocyclobutenes appear to be unreactive towards Ni(0) species [103], biphenylene adds to $Ni(PEt_3)_2(cod)$ giving rise to a dibenzonickelacyclopentadiene (Eq. (2.21)) [115]. A highly unusual oxidative C–C addition of hexakis(trifluoromethyl)benzene to Pt(0) is presented in Eq. (2.22) [116].



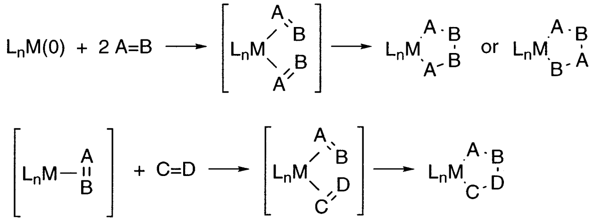
(2.21,2.22)

$Pt(0)L_n$ = $[Pt(t\text{-}BuNC)_3]_2$ or $Pt(PMe_3)_2(PhCH{=}CHPh)$.

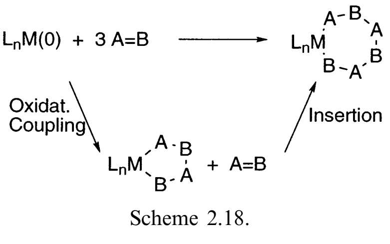
L = *t*-BuNC or PMe_3

2.4. Oxidative coupling (cycloaddition) of unsaturated molecules

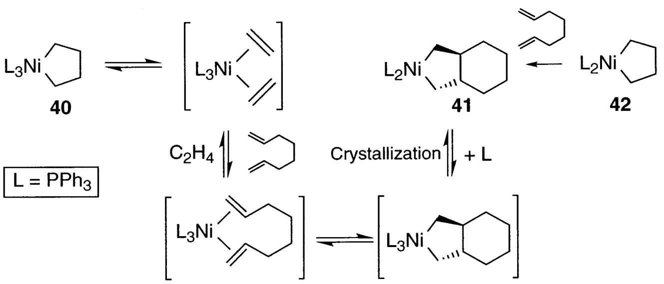
The cycloaddition of two (or more) unsaturated fragments to a metal unit frequently leads to metalacyclic species (Eqs. (2.23) and (2.24)). This is one of the most useful methods of metalacycle synthesis, since it gives access to relatively complex structures starting from small unsaturated molecules. In principle the reaction can take place on M(0) or M(II) centres to give, respectively, M(II) or M(IV) metalacycles. It may involve two identical (oxidative homocoupling, Eq. (2.23)) or different unsaturated units (oxidative heterocoupling, Eq. (2.24)). Although the formal cycloaddition of more than two fragments is also possible (Scheme 2.18), this process frequently consists of more than one elemental step, namely a true cycloaddition process followed by an insertion reaction.



(2.23,2.24)



Scheme 2.18.



Scheme 2.19.

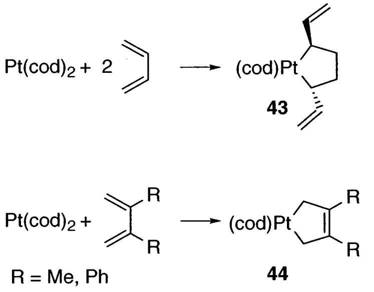
2.4.1. *Oxidative homocoupling*

The presence of electron withdrawing substituents on unsaturated molecules can ‘activate’ them towards their oxidative cycloaddition to nucleophilic M(0) centers. Structural strain is an additional factor that may favor that kind of process. In the following discussion, a separate treatment will be given for activated and unactivated substrates. It may be argued that the concept of substrate ‘activation’ is a rather subjective one, nevertheless we find it a very useful criterion for the organization of this section.

2.4.1.1. Homocoupling of unactivated alkenes, dienes, allenes and alkynes. The cycloaddition of unactivated unsaturated molecules to group 10 M(0) complexes is relatively unusual, although attending to the published reports its feasibility appears to increase in the order: alkenes, dienes $<$ alkynes $<$ allenes. Our survey will start with the alkene and diene homocoupling reaction, and then progress to the more facile cycloaddition reactions.

The decomposition of the nickelacyclopentane complex **40** is reversible, hence this pentacoordinated nickelacycle reacts with 1,7-octadiene stereoselectively leading to the stable *trans*-nickelahydrindane **41** with loss of one of the PPh_3 ligands (Scheme 2.19) [117]. Although orbital symmetry considerations indicate that such a process is only allowed in pentacoordinated species [118], square planar **42** also reacts with 1,7-octadiene directly giving **41**. In a similar fashion, the reaction of **40** with propene or norbornene was reported to give metalacycles [119], but these were not isolated.

The cycloaddition of 1,3-dienes is a very important process that takes place during their oligomerization or telomerization catalized by Ni(0) species [120,121]. A similar transformation occurs in the reaction of $Pt(cod)_2$ with 1,3-dienes, giving stable metalacyclic species [108,109]. The double bonds of butadiene can react independently, (Eq. (2.25)) to give the vinyl-substituted metalacycle **43** or they can be both involved in the reaction with $Pt(cod)_2$, to form a metalacycle of type **44**. The NMR spectra of the latter complexes indicate that they are true σ-platinacyclopentene metalacycles rather than π-diene complexes (Eq. (2.26)).

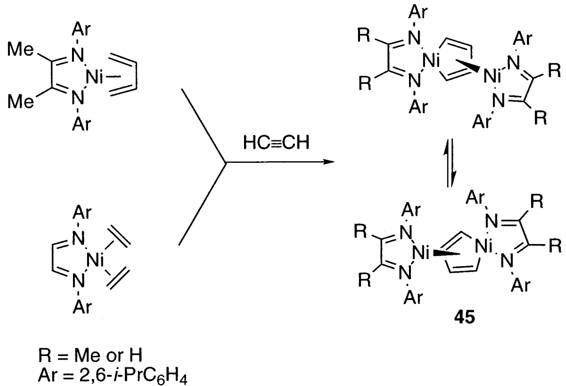


(2.25,2.26)

The reactions of diazadiene Ni(0) complexes with acetylene have been reported by tom Dieck [122] and Porschke [123,124] to produce mixed-valence complexes of type **45**, in which a metala(II)cyclopentadiene moiety binds a Ni(0)(diazabutadiene) fragment as a π-ligand (Scheme 2.20). A different binuclear derivative, containing a nickelacyclopentadiene unit and a bridging $HC\equiv CH$ molecule, has been obtained by reaction of $i\text{-}Pr_2PCH_2CH_2P\text{-}i\text{-}Pr_2$, ethyne and a Ni(0) complex [125].

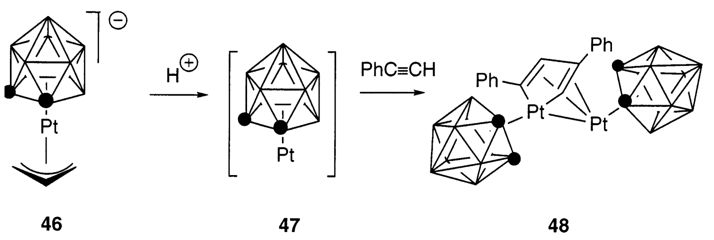
Interestingly, a platinum metalacyclic binuclear species, **48**, similar to **45**, can be obtained by reaction of phenylacetylene with the formally Pt(0) fragment $Pt(Me_2C_2B_9H_9)$, **47**, generated in situ by protonation of the allyl complex **46** (Scheme 2.21) [126].

The cycloaddition of allenes and other cumulenes seems to be a facile process. Thus, allenes react with Pt(0), or Ni(0) to give metalacycles such as **49** [108,109], **50** [127], **51** (L = dcpe [128] or bipy, phen [129]) or **52** [130]. The cumulene **53** reacts similarly with Ni(bipy)(cod) (Eq. (2.27)) [131].

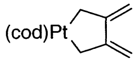


R = Me or H
Ar = 2,6-i-PrC_6H_4
or 2,6-Me-C_6H_4

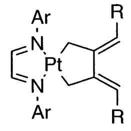
Scheme 2.20.



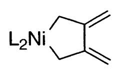
Scheme 2.21.



49

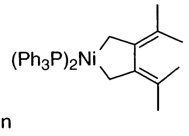


50

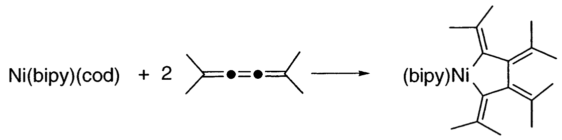


L_2 = dcpe, bipy, phen

51



52

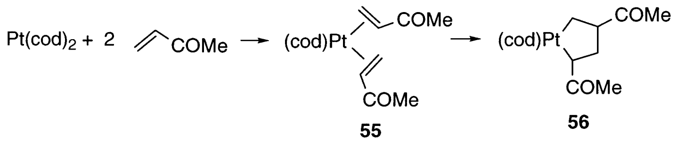


53 **54**

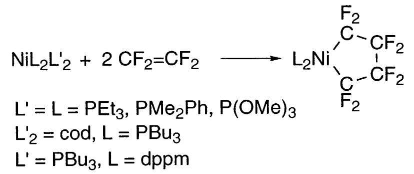
(2.27)

2.4.1.2. Oxidative homocoupling of activated substrates. Activated alkenes or alkynes react rapidly and irreversibly with many M(0) complexes of the Ni group. Although these reactions not always lead to metalacyclic products, their formation is frequently observed. Methylvinyl ketone is cyclodimerized by Pt(0) to give platinacyclopentane **56** through the intermediacy of the isolable bis-olefin complex, **55** (Scheme 2.22) [49].

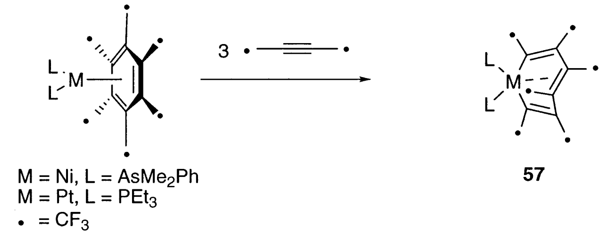
The oxidative coupling reactions of perfluoroethylene and hexafluorobutyne were studied by Stone in the early seventies as part of a more ample work on organometallic fluorocarbon derivatives, the first one leading to very stable perfluorometalacyclopentanes (Eq. (2.28)) [132]. In contrast with perfluoroethylene, hexafluoro-2-butyne is cyclotrimerized by Pt(0) and Ni(0) species, giving complexes of hexakis(trifluoromethyl)benzene [133,134]. The reactions of some of these Ni [134] and Pt [135] complexes of $C_6(CF_3)_6$ with a three-fold molar excess of hexafluoro-2-butyne gives metalacyclic species of type **57** (Eq. (2.29)). $Ni(H)(Cl)(PCy_3)_2$ and $NiCp_2$ also react with this fluoroalkyne to give metallacyclic species [136,137].



Scheme 2.22.

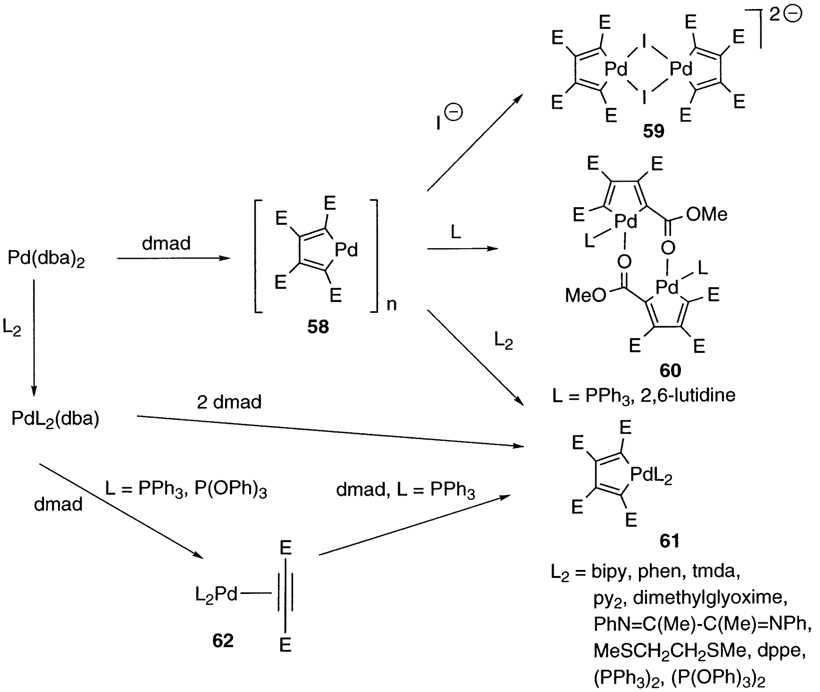


(2.28)



57

(2.29)



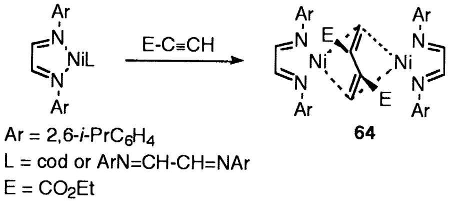
Scheme 2.23.

Due to its involvement in different oligomerization and co-oligomerization catalytic reactions [138], the oxidative cycloaddition of acetylenic esters such as dimethylacetylenedicarboxylate (dmad) to Ni, Pd and Pt has received much attention. The study of the catalytic cyclotrimerization of dmad by Pd(dba)$_2$ led almost simultaneously to Maitlis [139,140] and Ito [141] to the discovery of the 'base-free' palladacyclopentadiene **58**, formed in the reaction of dmad with Pd(dba)$_2$ (Scheme 2.23). Complex **58** reacts with a wide range of donor ligands [139–143a] to give soluble discrete molecules, **59**–**61**. Palladium (0) complexes generated in situ from

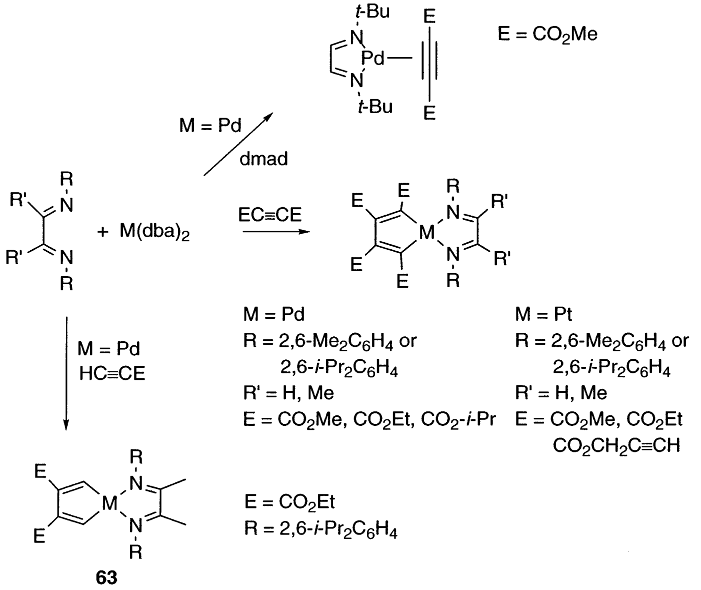
$Pd(dba)_2$ and nitrogen donor ligands also react with dmad to give the same palladacyclopentadiene adducts obtained from **58** [139–141]. The phosphorus ligands PPh_3 or $P(OPh)_3$ allow the isolation of the corresponding π-complex **62**, which can react further to give **61** only in the former case [141]. On the basis of these results, it has been proposed that the ability to couple two alkyne molecules decreases with the π-acceptor ability of the ancillary ligands (i.e. bipy ≈ phen ≫ $PPh_3 > P(OPh_3)$) since the latter can stabilize the alkyne π-complex.

The use of diazabutadiene ligands in the oxidative coupling of alkynes has been studied in detail by tom Dieck [142,144a] who has determined the scope of the reaction. As shown on Scheme 2.24, the cycloaddition of dialkyl acetylenedicarboxylates takes place with $Pd(dba)_2$ and diazabutadiene ligands containing aromatic substituents on the nitrogen atoms. Bulky alkyl substituents, such as *t*-Bu give the corresponding π-alkyne complex. Very low yields of the palladacyclopentadiene complex **63** (Scheme 2.24) were obtained when dmad was substituted by ethyl propiolate, and less activated alkynes failed to provide any metalacyclic product. Platinum follows a similar trend, and the reaction of $Pt(dba)_2$, with a diazabutadiene ligand and dmad gave the corresponding metalacycles [142,143b].

The reactivity of acetylenic esters towards diazadiene complexes of nickel (0) contrasts with that of its heavier neighbours. A binuclear complex **64** has been isolated from the reaction of $Ni(diazadiene)_2$ or Ni(diazadiene)(cod) and ethyl propiolate (Eq. (2.30)) [144b].



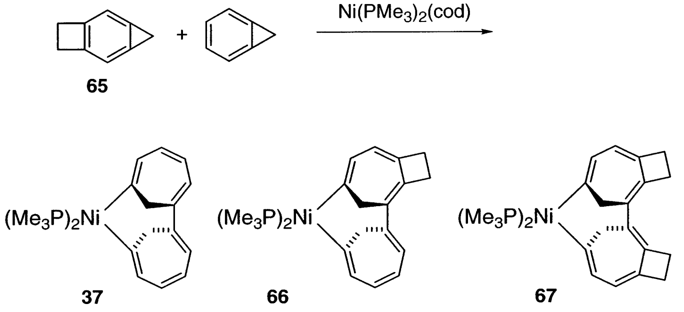
(2.30)



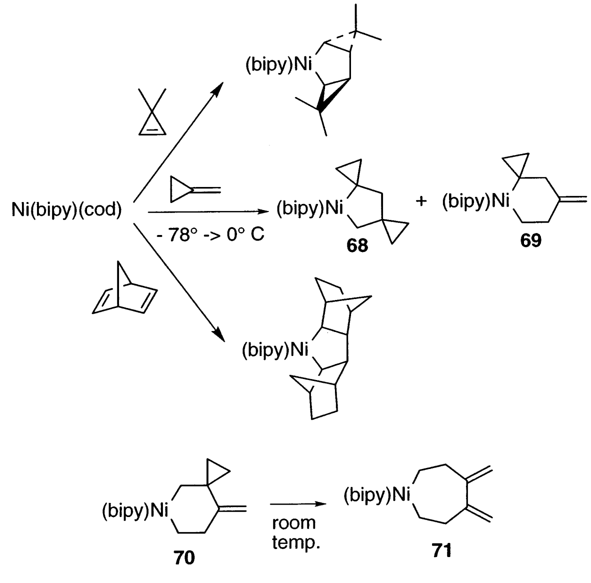
Scheme 2.24.

Besides electron deficiency, structural strain can also lead to the activation of an unsaturated molecule towards the cycloaddition reaction. Following Wilke's work on the activation of cyclopropabenzene by the $Ni(PMe_3)_2$ fragment [102] (see Scheme 2.14), Vollhardt [103] has shown that the highly strained hydrocarbon **65** reacts with $Ni(PMe_3)_2(cod)$ forming **67**. Although cyclopropabenzene is clearly less strained than **65**, the reactivity of both hydrocarbons toward Ni(0) is not very different, as shown by the competition experiment depicted in Eq. (2.31). This result, although intuitively surprising, is in accord with MNDO calculations, which reveals similar energies and coefficients of the frontier orbitals in both hydrocarbons

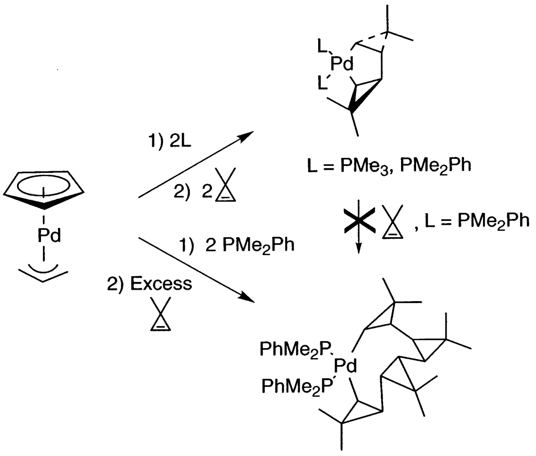
The oxidative coupling of strained double bonds is, however, more commonly observed than the σ-C–C cycloaddition mentioned above. Thus, Binger has studied



37:66:67= 4:4:1 (2.31)



Scheme 2.25.



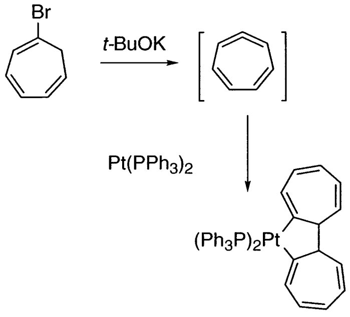
Scheme 2.26.

(Scheme 2.25) the reaction of norbornadiene and cyclopropenes with Ni(bipy)(cod) [145–147]. The reaction of methylenecyclopropane with Ni(bipy)(cod) is complex and may give different products depending on the reaction conditions [147]. If the temperature of the reaction mixture is kept below 0°C, the nickelacyclopentane **68** is formed as the main product, together with small amounts (ca. 8%) of a different metalacycle for which structure **69** was tentatively proposed. At room temperature, a mixture of **68**, **70** and small amounts of **69** was obtained. Complex **70** is thermally unstable and isomerizes to **71** upon standing in solution at room temperature.

Scheme 2.26 shows some transformations of the in situ generated 'Pd$(PR_3)_2$' fragment [148].

The cycloaddition of cyclopropenes to Pd(0) complexes can be highly stereoselective. The introduction of asymmetric substituents in the cyclopropene ring leads to the formation of one diastereoisomer in high (> 90%) e.e. [149].

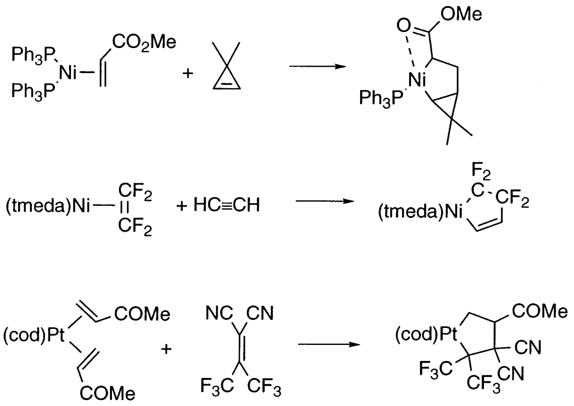
Cycloheptatetraene, an unstable cycloallene, may be generated from bromocycloheptatriene, and has been trapped by the Pt$(PPh_3)_2$ fragment (Scheme 2.27) [150]. The regioselectivity of this reaction is the opposite to that observed in the cycloaddition of allene at Ni and Pt centers (cf. compounds **49**–**52**).



Scheme 2.27.

2.4.2. Oxidative heterocoupling

Although the reaction of a mixture of two unsaturated substrates with M(0) complexes may lead to their heterocoupling and hence to unsymmetrical metalacycles, this procedure would afford, in general, mixtures of homo- and heterocoupled products, as for example in Eq. (2.31). However the heterocoupling may be effected in a selective manner by reacting a π-complex that contains one of the unsaturated substrates with the second one. As shown in Eqs. (2.32) [151]; (2.33) [152] and (2.34) [49], olefin or alkyne complexes may serve for this purpose.



55

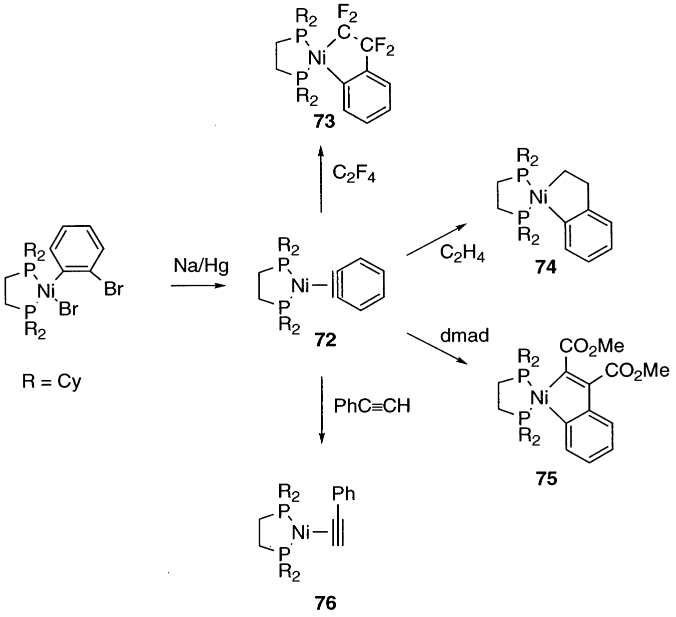
(2.32,2.33,2.34)

This approach is specially useful when one of the unsaturated molecules to be cyclodimerized is an unstable species that can be generated in the coordination sphere of a transition metal (e.g. benzyne or other arynes). Bennett has developed the synthesis of nickel group complexes of benzyne and other cycloalkynes, which is partly covered by a review article [153]. A more recent review on complexes of arynes and other strained ligands has appeared [154].

Benzyne or naphthalyne complexes of nickel can be prepared by reduction of the corresponding 2-bromoaryl derivatives with sodium amalgam [155–158], as shown in Scheme 2.28. These complexes can react with unsaturated molecules, such as tetrafluoroethylene [158,159], ethylene [155], or alkynes [155], giving rise to the metalacycles **73**, **74** and **75**, respectively. The isolation of the latter complex is unusual since in general, this kind of reaction leads to substituted naphthalenes [157,160].

The reactivity of some platinum-cycloalkyne complexes resembles somewhat that of the nickel-aryne derivatives. As shown in Scheme 2.29, minor structural changes can shift the course of their reaction with tetracyanoethylene towards heterocoupling or to a ligand exchange followed by cyclotrimerization [161].

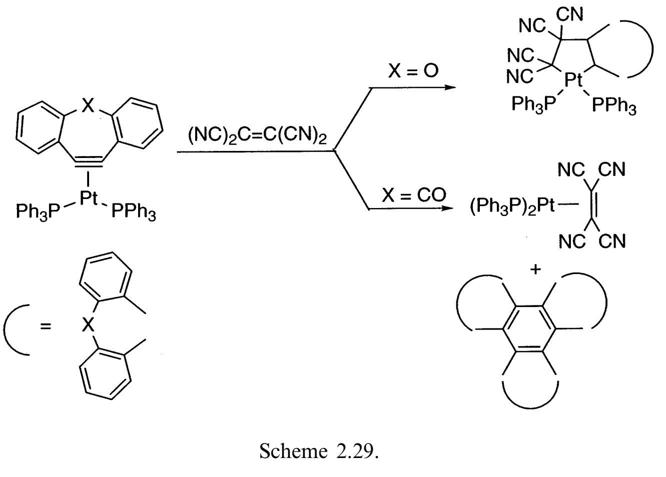
Alkyne complexes of palladium of type **77** are considered intermediates in the catalytic cyclotrimerization of alkynes catalyzed by diazabutadiene-bearing palladacyclopentadienes (Scheme 2.30). Even though they are rather elusive species [144], they can be readily trapped into catalytically inert metalacycles of type **78** if appropriate allenes are added to the reaction mixture [162]. Certain olefins can also



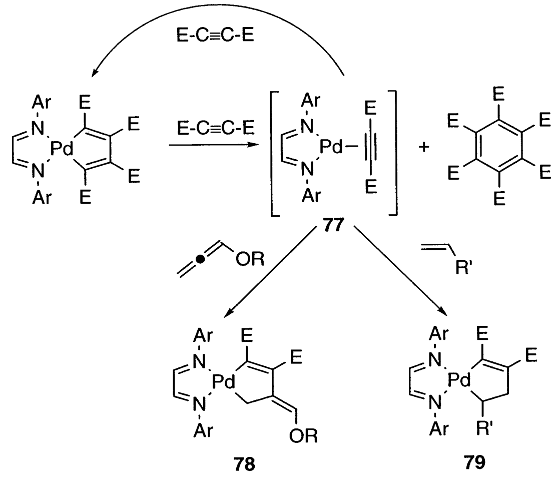
Scheme 2.28.

react with the palladium-alkyne intermediate, giving palladacyclopentenes of type **79** [163]. However, a very large excess of the olefin was required (ca. 250-fold), presumably in order to compete efficiently with the more reactive alkyne dmad.

Although the reaction of CO and isocyanides with alkyne complexes usually consists in a simple ligand exchange process, in some cases cycloaddition can be observed. Hoberg has reported that the bipyridyl-alkyne complex **80** reacts with two equivalents of carbon monoxide to give a metalacyclic complex of type **81**

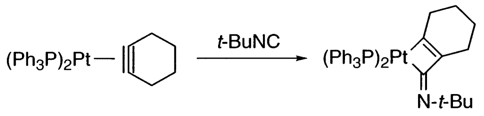


Scheme 2.29.

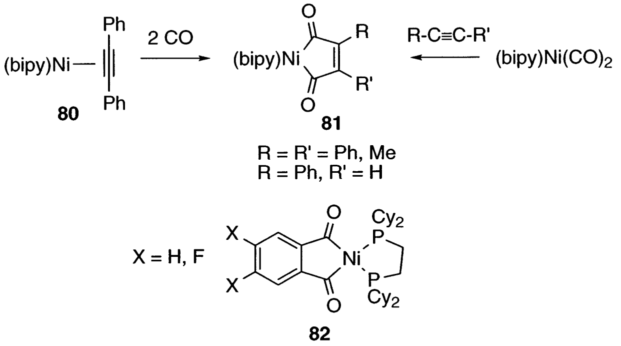


Scheme 2.30.

(Scheme 2.31) [112]. Complexes of type **81** can also be conveniently obtained by reaction of $Ni(CO)_2(bipy)$ with alkynes [114]. Bennett has observed a similar reaction between nickel-benzyne derivatives and carbon monoxide, but the products, **82**, could not be isolated [164]. The same author has also reported the reaction of a platinum cyclohexyne complex with one equivalent of *t*-BuNC, which gives a platinacyclobutene ring (Eq. (2.35)) [165].



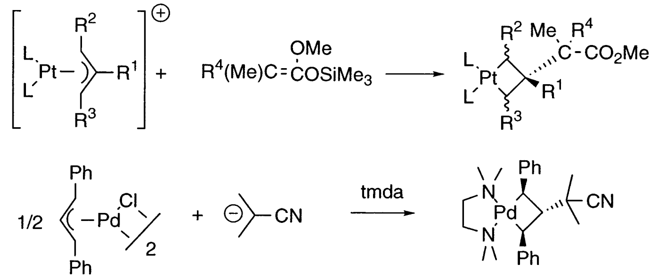
(2.35)



Scheme 2.31.

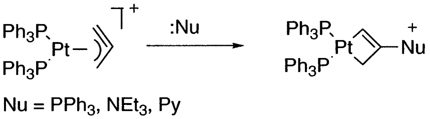
2.5. Nucleophilic attack on coordinated ligands

The attack of a nucleophile on a π-allyl complex can take place on the central carbon atom, to give a metalacyclobutane, or on a terminal atom, yielding in this case a metal-olefin complex. As predicted by the rules of Davies, Green and Mingos, the latter regioselectivity is favored under thermodynamic control conditions, however, there are some reports on the preparation of stable metalacyclobutanes by the reaction of platinum [166,167] (Eq. (2.36)) or palladium [168] (Eq. (2.37)) allyl derivatives with nucleophiles. In accord with theoretical calculations [167,169] the experimental evidence indicates that the regioselectivity of the attack is highly influenced by the nature of both the nucleophile and the ancillary ligands present in the complex. Attack on the central carbon is kinetically favored by sterically hindered and basic nucleophiles [167,168] and also by good σ-donor coligands [169], while stabilized carbanion nucleophiles and π-acceptor ligands tend to favor attack on the terminal carbon atom.



(2.36,2.37)

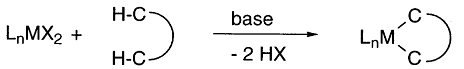
The attack of a nucleophile on the central carbon atom of η^3-propargyl complexes can proceed to give a metalacyclobutene ring [169]. However, in the case of platinum or palladium this process is complicated by subsequent hydrogen-transfer reactions that lead to π-trimethylene [170], π-oxatrimethylene [171,172] or π-azatrimethylene [173] complexes, which exceed the scope of this review. Metalacyclobutene-type metalacycles can be obtained if the attacking nucleophile lacks any exchangeable hydrogen atom, as shown in Eq. (2.38) [174].



(2.38)

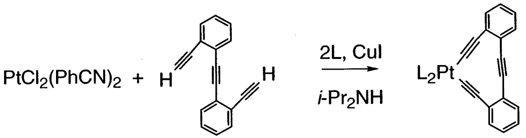
2.6. Miscellaneous synthetic methods

A procedure that can be formally identified with the transmetalation method is the treatment of a metal dihalide complex with dibasic carbon acids in the presence of an appropriate base, as shown in Eq. (2.39). The relationship between these transformations and the transmetalation reaction is only formal and rather differ-



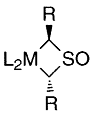
(2.39)

ent mechanisms (i.e. cyclometalation) may be involved. This procedure has allowed the synthesis of the platinum macrocycle **83**, [175] (Eq. (2.40)). The intermediacy of a copper alkynyl species that can act as a transmetalation reagent appears obvious. Kemmitt prepared a large number of heterometalacyclobutanes of type **84** [52], **85** [52] and **86** [176] starting from sulphoxides, sulphones or phosphine oxides, using silver oxide or carbonate as bases. Interestingly, although the metalathietane-3,3-dioxides **85** are also readily available by the transmetalation method (see Eq. (2.8)), attempts to synthesize **84** from dilithiated sulphoxides failed [177].



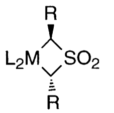
83

(2.40)



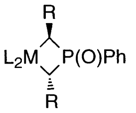
84

M = Pt
L = PPh_3, PMe_2Ph, $PPhMe_2$
R = COPh



85

M = Pd, Pt
L = tertiary phosphine
R = COPh or CO_2Me

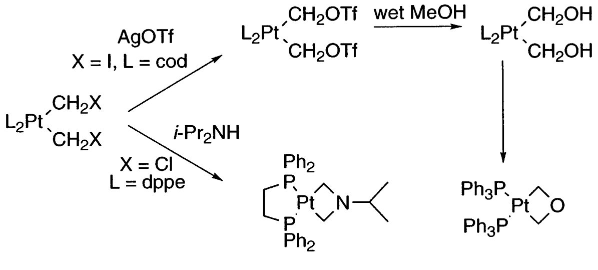


86

M = Pt
L = cod, tertiary bidentate or monocentate phosphine
R = COPh

Other heteroplatinacyclobutanes containing nitrogen [178] or oxygen [179] atoms in the ring have been prepared by nucleophilic substitution reactions on bis(dihalomethyl)platinum complexes, as shown on Scheme 2.32.

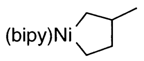
Some nickelacyclopentanes can be prepared by oxidative addition of 1,4-dibromoalkanes to Ni(cod)(bipy) or Ni(cod)(phen) (Eq. (2.41)). Reported as early as 1976 [180], this reaction has been extended recently by Hillhouse for the synthesis of substituted nickelacyclopentanes **87** and **88** as well as benzo-



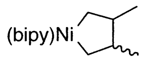
Scheme 2.32.

[c]nickelacyclopentene **89** [181,182]. A related reaction is the oxidative addition *o*-diiodobenzene to $Ni(CO)_4$, which affords the polymeric Ni(IV) metalacycle **90**, [183] (Eq. (2.42)).

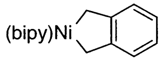
(2.41)



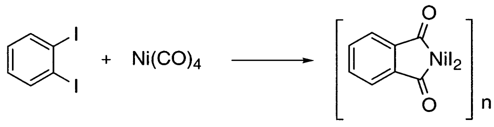
87



88



89



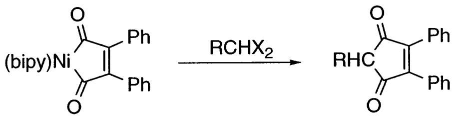
90

(2.42)

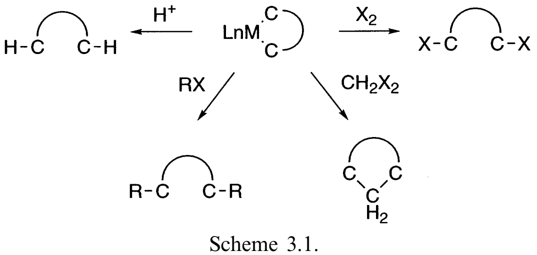
3. Reactions of group 10 metalacycles

3.1. Electrophilic attack on metalacycles

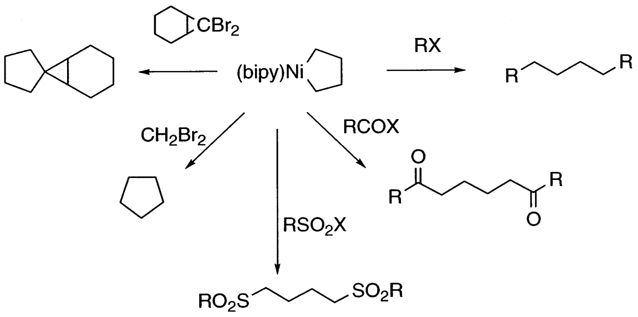
The interaction of metalacycles with electrophilic reagents such as protic acids, halogens or alkyl halides gives, respectively, hydrocarbons, α,ω-dihaloalkanes or hydrocarbons resulting from double C–C coupling reactions (Scheme 3.1). Since these products are easily detected and identified, the reactions shown in Scheme 3.1 have been frequently used as a simple characterization method (see, for example, Refs. [19, 21, 27, 70, 102, 112, 114, 115, 117, 140 and 181]), especially in a time when many actually widespread NMR techniques were not available, or when the metalacycles (sometimes formed as minor components of mixtures [54]) were unstable and difficult to handle. Besides their utility as a characterization tool, some of these reactions have an obvious potential in organic synthesis, since they provide a method for the formation of new C–C or C–X bonds. Some pertinent examples are shown on Scheme 3.2 [180] and Eq. (3.1) [114].



(3.1)

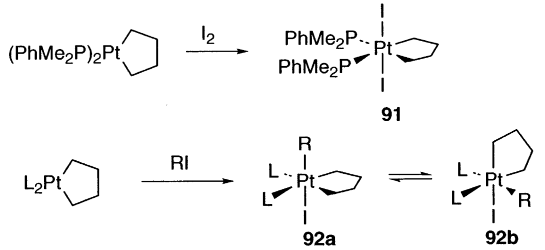


Scheme 3.1.



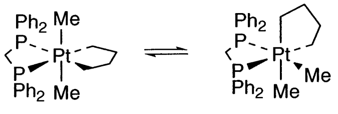
Scheme 3.2.

The reaction of metalacycles with alkyl halides may be considered in the more ample context of the group 10 metals mediated C–C coupling reactions. This process is involved in some important reactions, such as the Pd catalyzed Stille coupling, nowadays a standard tool in organic synthesis. This author studied the reaction of platinum alkyls with alkyl halides, and found that an oxidative addition takes place, giving a Pt(IV) complex, which can decompose by reductive elimination, giving rise to C–C coupling products [184]. Since the + 4 oxidation state is common for Pt, a large number of Pt(IV) alkyl complexes have been prepared by this procedure [185,186]. These include metalacyclic species, which were generated by reaction of platinacyclopentanes with halogens (Eq. (3.2)) [187] or alkyl halides (Eq. (3.3)) [188,189]. The latter complexes exist as a mixture of isomers, **92a** and **92b**. The same stereochemical equilibrium was observed in complexes **93a** and **93b**, prepared by alkylation of **92a**/**92b** (L_2 = dppm, R = Me) with MeLi [189].



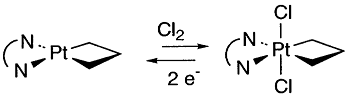
L_2 = dppm, R = Me; L_2 = bipy, R = Et

(3.2,3.3)

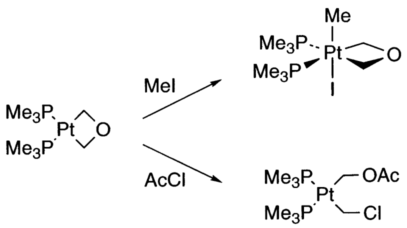


93a **93b**

The oxidative addition of halogen can be reversed by reduction of the platinum(IV) metalacycle dihalide, either chemically or electrochemically (Eq. (3.4)) [190].



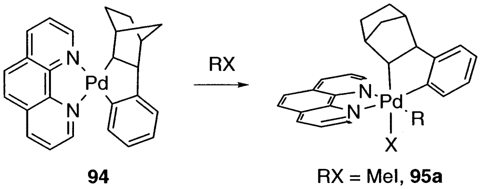
(3.4)



Scheme 3.3.

The presence of a heteroatom in the ring introduces a second nucleophilic center that can compete with the metal in the reaction with electrophiles. An example is shown in Scheme 3.3. The weak electrophile MeI attacks the 'soft' metal center, while the attack of acetyl chloride to the 'hard' oxygen atom is kinetically favored, giving a ring-opened product [191].

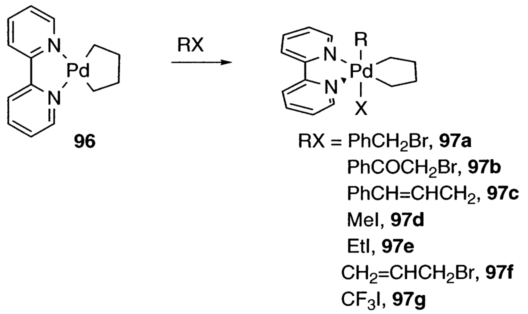
Despite the involvement of Pd(IV) organometallics in catalytic processes, the chemistry of these compounds has only recently started to develop. Palladium metalacycles supported by rigid nitrogen ligands such as bipy or phen react with alkyl halides giving some of the first Pd(IV) complexes stable enough to be isolated and characterized. These compounds were prepared by Catellani [74,192–194] and Canty [195,196] from the Pd(II) metalacycles **94** and **96**, respectively, and different alkyl halides (Eqs. (3.5) and (3.6)). While the more crowded metalacycles **95** adopt a conformation with R and X occupying mutually *cis* positions, most of the palladacyclopentane derivatives **97** prefer the more symmetrical conformation with R *trans* to X, except for **97b**, which was found to exist in solution as a mixture of the two possible isomers. The use by Canty and co-workers of rigid, tripodal ligands such as tris(pyrazolyl)borate (Tp) allows the preparation of very stable Pd(IV) metalacyclopentanes, by oxidative addition of alkyl halides [195,197], halogen or halogen sources or water [198,199]. (Scheme 3.4). Surprisingly, the oxidative addition of water gives rise to the hydroxopalladium (IV) complex **99** together with H_2. A theoretical analysis at the MP2//SCF level of the latter process [200] has shown that the Tp ligand actively participates assisting the oxidative addition of water and the protonation of the resulting Pd(IV) hydride-hydroxo species to form the final product (Scheme 3.4). The same hydroxide complex can be obtained by oxidation of the Pd(II) metalacycle **98** with hydrogen peroxide. The hydroxo ligand of **99** can form hydrogen bonds with phenols, which have been structurally characterized [201].



94

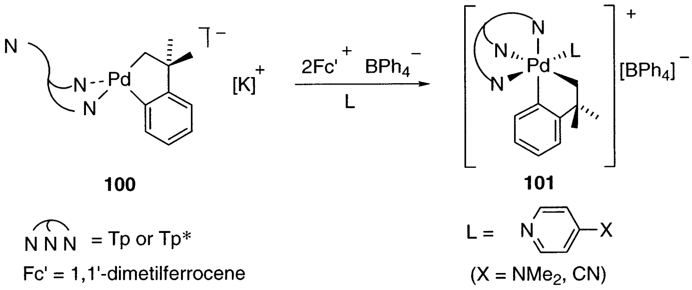
RX = MeI, **95a**
$CH_2{=}CHCH_2Br$, **95b**
$NO_2C_6H_4CH_2Br$, **95c**

(3.5)

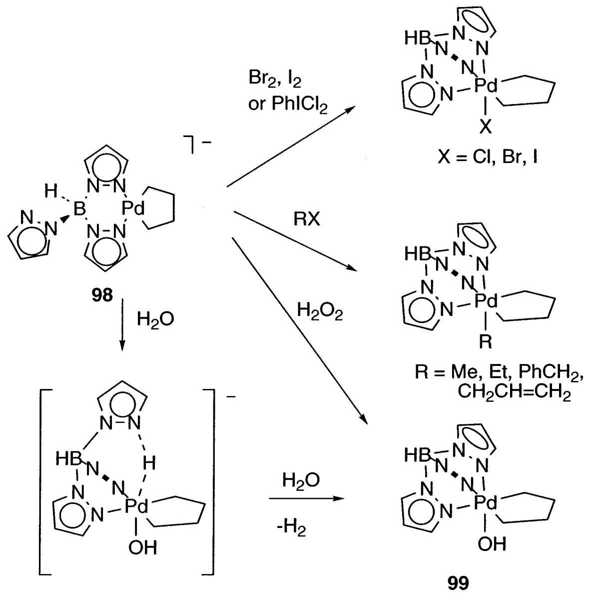


(3.6)

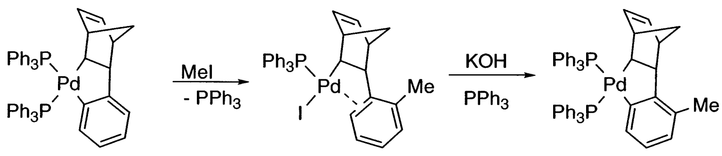
In the above line of reasoning, the oxidative addition of halogen or alkyl halides to the anionic palladabenzo[b] cyclopentene complex **100**, stabilized by Tp or Tp* (Tp* = tris(2,5-dimethyl)pyrazolylborate) gives similar results, affording stable Pd(IV) metalacyles. The anion **100** can also be oxidized by ferricinium salts in the presence of substituted pyridines, giving the cationic adducts **101** (Eq. (3.7)) [80].



(3.7)

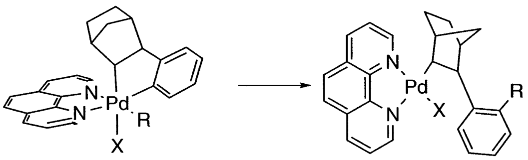


Scheme 3.4.



Scheme 3.5.

In the next section, it will be shown that the decomposition of Pd(IV) metalacycles involves a reductive elimination process that leads to Pd(II) species. For metalacycles that contain at least one M-aryl bond, such as **95**, this process is highly selective and affords quantitatively Pd(II) alkyl derivatives resulting from ring-opening by alkyl-aryl coupling (Eq. (3.8)) [74,193]. Cheng [79] has taken advantage of this process, achieving an overall aromatic substitution process at Pd(II) metalacycles (Scheme 3.5).



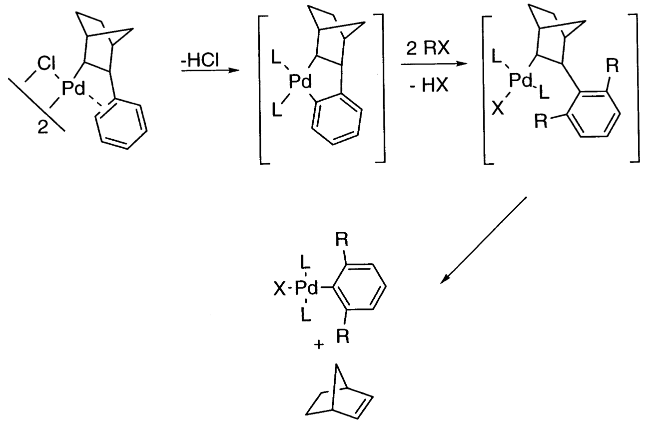
95

X = I, R = Me
X = Br, R = $CH_2CH{=}CH_2$
X = Br, R = $CH_2C_6H_4NO_2$

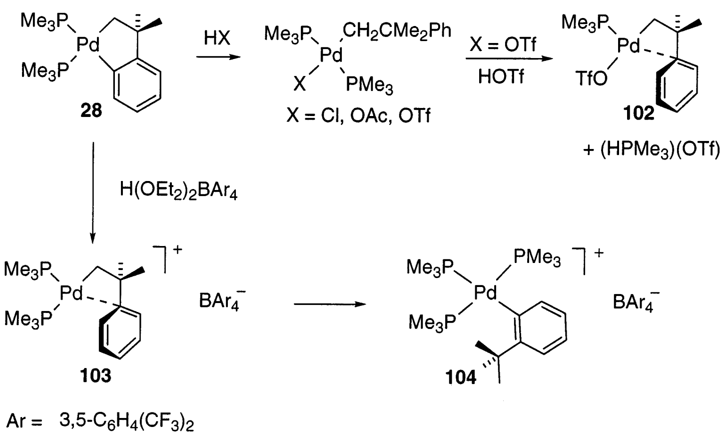
(3.8)

In turn, Catellani has shown that the doubly alkylated product that forms in the way shown in Scheme 3.6 is unstable and decomposes through a β-C–C cleavage process [202].

The reaction of group-10 metalacycles with one equivalent of a protic acid frequently cleaves one metal–carbon bond in a selective manner. Thus, the Ni–aryl bond of the nickelacyclopentene **1** can be selectively cleaved even by weak carbonic acid [11,12]. The analogous Pd metalacycle, **28**, displays a similar behavior, the Pd

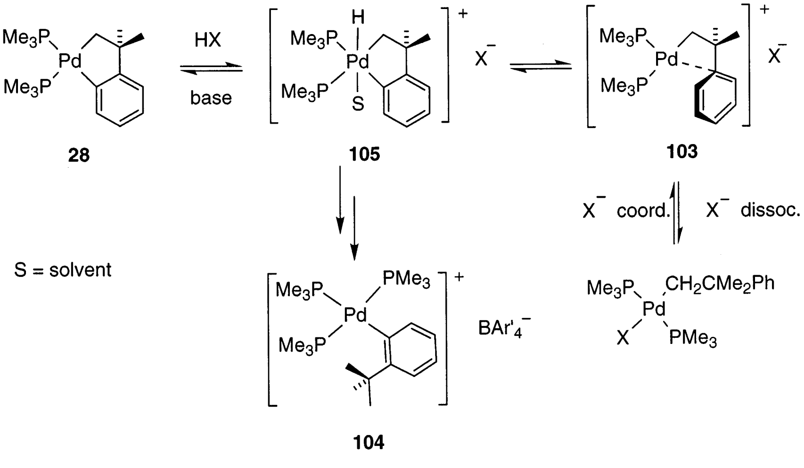


Scheme 3.6.

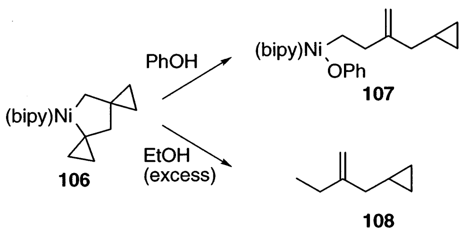


Scheme 3.7.

aryl bond being attacked by AcOH or HCl (Scheme 3.7). This is the reverse of the cyclometalation reaction by which this metalacycle is formed, hence the protonation with acids whose conjugated bases are anions of low coordination ability may provide some hints on the mechanism of the intramolecular C–H activation [81]. Thus, the reaction of **28** with two equivalents of triflic acid (HOTf) does not cleave both Pd–carbon bonds, instead it gives the η^1-arene complex **102**, along with phosphonium triflate. This reaction illustrates the tendency of the aryl group to coordinate to Pd, facilitating the intramolecular C–H bond activation. However, **102** is very stable and cannot be readily cyclometalated. The protonolysis of **28** with the acid $[H(OEt_2)_2][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$ gives the cationic η^1-arene **103**. At variance with the behavior found for **102**, **103** spontaneously rearranges to **104** in donor solvents such as Et_2O (Scheme 3.7). It has been proposed that this rearrangement



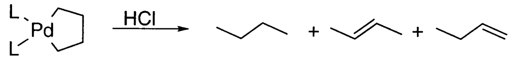
Scheme 3.8.



Scheme 3.9.

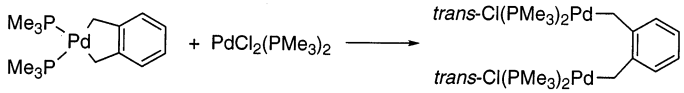
takes place by means of an intramolecular C–H activation process that may involve the Pd(IV) hydride intermediate **105** (Scheme 3.8). Therefore, the presence of a positive charge on the Pd center appears to be important in the C–H activation reaction. It is likely that the cyclometalation of neophylpalladium derivatives by an external base involves the deprotonation of the hydride **105**, formed by dissociation of an anionic X^- ligand, as shown in Scheme 3.8.

In some cases, the protonation of a metalacycle may render a ring-opened product which is unstable toward further rearrangements. An example is shown in Scheme 3.9 [129], where the addition of one equiv of phenol to the nickelacyclopentane **106** causes the selective cleavage of the Ni-quaternary C bond. However, the kinetic product of the protonation contains a cyclopropyl ring in the β-position that is immediately cleaved by the metal, giving **107**. The complete alcoholysis of **106** with ethanol gives the hydrocarbon **108**, which must be formed by protonation of an intermediate analogous to **107**. In a similar fashion, the instability of intermediate butyl-palladium species with respect to β-elimination can explain the formation of butenes in the protonolysis of palladacyclopentanes with HCl (Eq. (3.9)) [21].



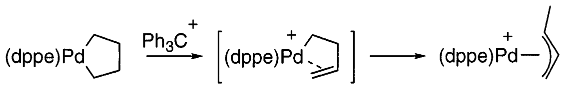
(3.9)

Besides RX, HX or X_2, other electrophiles can also react with group 10 metalacycles giving different open-chain products. Metal dihalide complexes can behave as electrophiles, giving alkanediyl-bridged complexes (Eq. (3.10)) [26].

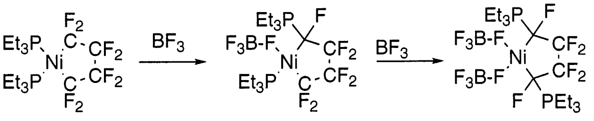


(3.10)

The triphenylmethyl cation acts as a strong Lewis acid and abstracts a hydride from the β position of palladacyclopentanes. The formed Pd(II)-alkene complex immediately rearranges to a cationic allyl (Scheme 3.10) [21]. A formally related process is



Scheme 3.10.



Scheme 3.11.

the α-fluoride abstraction by BF_3 from a perfluoronickelacyclopentane, which results in the formation of ylide species (Scheme 3.11), presumably through the intermediacy of a fluorocarbene complex [203].

3.2. Decomposition and rearrangement reactions

The last stage in the mechanism of every synthetically useful catalytic or stoichiometric reaction in which a metalacycle is involved, is its decomposition to give the desired organic products. The understanding of this process is therefore of paramount importance in the design of new applications of metalacycles. This is an aspect of the chemistry of metalacycles which differs considerably from that of their open-chain analogs. A typical decomposition process for group-10 dialkyl complexes is the β-elimination, which requires a transition state in which the dihedral angle M–C–C–H must be nearly 0° [15,16]. This transition state cannot be achieved readily in medium or small ring-sized metalacycles, therefore β-elimination is comparatively more hindered in metalacyclobutanes, metalacyclopentanes or metalacyclohexanes. Other frequently observed decomposition process in dialkyls, reductive elimination, is less favorable, thermodynamically, in small metalacycles since it leads to strained organic products (i.e. cyclopropanes or cyclobutanes). With these two decomposition pathways partially blocked, metalacycloalkanes are considerably more stable than related dialkyls, and, as discussed in the preceding sections, a large number of group 10 metalacyclobutanes, metalacyclopentanes or metalacyclohexanes have been isolated and characterized, in contrast with the low stability of the corresponding diethyl or di-*n*-butyl derivatives [15,16,204–206]. Nevertheless, other decomposition processes, such as α-elimination or retro-cycloadditions may take place (Fig. 1). As expected, large ring metalacycles display stabilities that are comparable to those of open dialkyls [16,148].

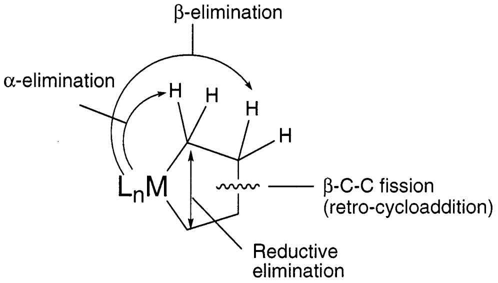
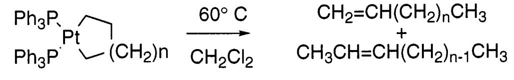


Fig. 1. Decomposition pathways in metalacycloalkanes.

3.2.1. Decomposition of M(II) metalacycles

Extensive studies on the decomposition mechanism of platinum and nickel metala(II)cycloalkanes have been carried out by Whitesides [15,16,23,207–209], Grubbs [17–19,48,117] and Miyashita [70], while Diversi has examined the decomposition of palladacyclopentanes [22].

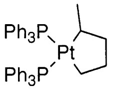
The thermolysis of platinacycloalkanes **109a**–**109c** with ring sizes larger than 4 takes place in dichloromethane at 60°C giving mixtures that contain 1- or 2-alkenes as the main organic products (Eq. (3.11)) [15,16]. As for the corresponding diethyl



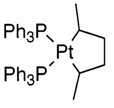
(3.11)

n = 1, **109a**; 2, **109b**;
3, **109c**

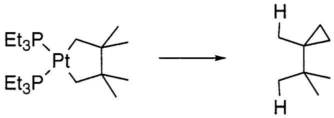
or dibutyl complexes, these products could form in a β-elimination-isomerization process. However, as attested by their high thermal stability, attaining the optimal geometry of the β-elimination transition state for the decomposition of **109a** and **109b** requires considerable strain. Moreover, since the α-substituted derivatives **2** and **3**, which bear H atoms more accessible to β-elimination, rearrange with comparable rates it is not clear that this mechanism plays a role in the thermal decomposition of this kind of metalacycle. A chain reaction with hydride transfer (the cyclometalation of a coordinated phosphine ligand could be the source of the Pt–H intermediate) was also proposed [15,16], and this has been invoked to explain the decomposition of some deuterium-labeled platinacyclopentanes [208]. This same mechanism could also account for the decomposition of the metalacycle **5** shown in Eq. (3.12) [23].



2



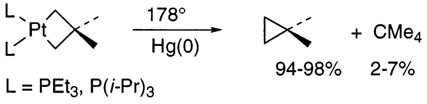
3



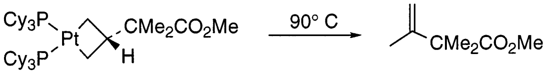
5

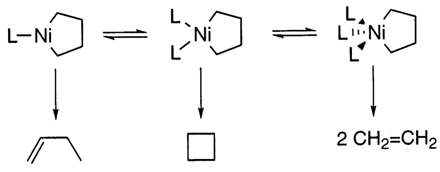
(3.12)

Whitesides has also studied the thermolysis of Pt(II) metalacyclobutanes with and without β-hydrogen atoms (Eqs. (3.13) and (3.14)) [23,166].



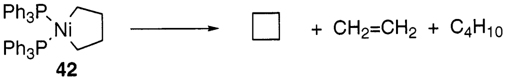
(3.13,3.14)





Scheme 3.12.

The decomposition of nickelacyclopentanes is considerably more complex than that of their platinum analogs [17–19]. Thus, the thermolysis of triphenylphosphine derivative **42** at 9°C gives cyclobutane, ethylene and butenes (Eq. (3.15)), clearly



42

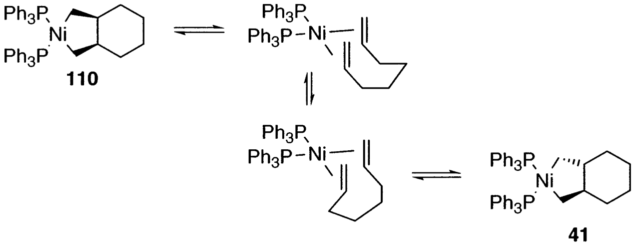
(3.15)

indicating that at least three different decomposition mechanisms operate in competition. As shown in Scheme 3.12, each of these mechanisms is connected with a coordination number of the metal. Orbital symmetry considerations [118], as well as more advanced calculations [210,211], support this decomposition pattern, although the possible involvement of tetrahedral intermediates cannot be ruled out.

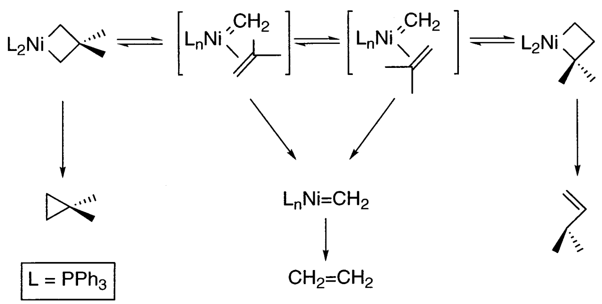
The β-C–C cleavage of metalacyclopentane derivatives of Ni to give two unsaturated fragments has also been observed. Thus, the skeletal rearrangement of the *cis*-nickelahydrindane **110** to the more stable *trans* isomer **41** is thought to proceed by retro-cycloaddition of octadiene, which then stereospecifically adds to the metal with *trans* configuration (Scheme 3.13) [117]. This decomposition route also appears to play a major role on the decomposition of nickelacyclobutanes [48] or nickelacyclohexanes [70].

A C–C fission process appears to be responsible for the decomposition of some four-member (Scheme 3.14) [70] and six-member (Scheme 3.15) [48] metalacycles, and also for that of the nickelacyclobutane $\overline{\mathrm{Ni}(\mathrm{CH_2CH_2CH_2})}$ when irradiated at $\lambda \geq 550$ nm in an argon matrix [97].

Although less studied than the corresponding nickela- or platinacycloalkanes, the decomposition of the corresponding palladium derivatives seem to be midway

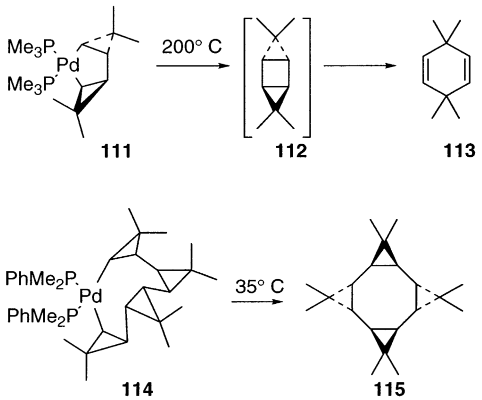


Scheme 3.13.



Scheme 3.14.

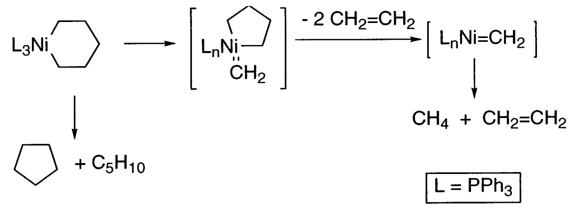
between them. Both β-elimination (to give butenes) and reductive elimination to cyclobutane are the main processes responsible for the decomposition of palladacyclopentanes [22]. In turn, 2,2-dimethylpalladacyclobutanes [70] decompose by reductive elimination to give 2,2-dimethylcyclopropane, but in none of these cases were detected significant amounts of ethylene or of products resulting from β-C–C cleavage. The extremely rigid palladacyclopentane **111** undergoes readily reductive elimination. The rigid carbon skeleton of this metalacycle disfavors other decomposition pathways, and it only decomposes at high temperatures giving the strained cyclobutane **112** that under the pyrolysis conditions rearranges to **113** (Eq. (3.16)). The ready decomposition of the macrocyclic complex **114** to the relatively unstrained hydrocarbon **115** contrasts with the stability of **111** (Eq. (3.17)) [148].



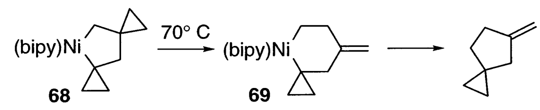
111 **112** **113**

114 **115**

(3.16,3.17)

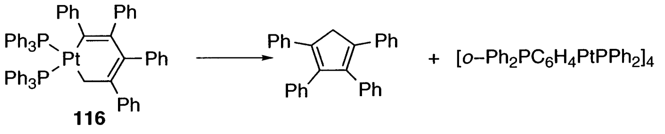


Scheme 3.15.



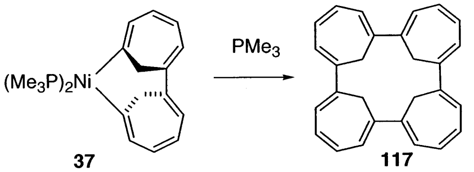
Scheme 3.16.

For metalacycles larger than five-membered, particularly for those where at least one of the carbon atoms attached to the metal center has an sp^2 hybridization, reductive elimination is extremely facile. A rare example of this type of metalacycle is the platinum derivative **116**, which readily decomposes in hot C_6D_6 giving tetraphenylcylopentadiene (Eq. (3.18)) [116].

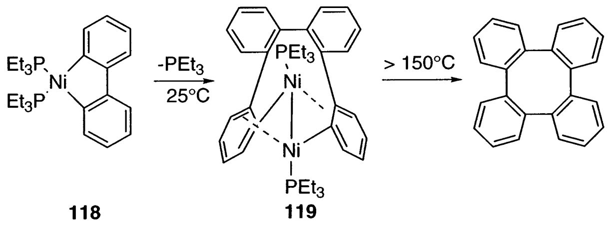


(3.18)

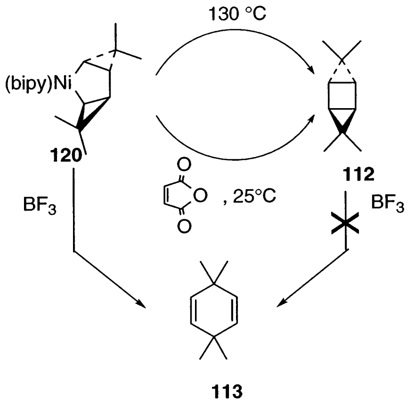
The thermolysis of some Ni metalacycles gives products whose nature evinces some type of rearrangement prior to reductive elimination. Thus, the nickelacyclopentane **68** experiences a ring expansion to **69** before reductive elimination takes place (Scheme 3.16) [129], whilst the formation of the cyclic hydrocarbon **117** suggests the intermediacy of a binuclear nickel complex (Eq. (3.19)) [101]. This intermediate might be similar to **119**, which is formed when the dibenzometalacycle **118** is allowed to stand in solution at room temperature. Complex **119** decomposes above 150° in tetraphenylene and metallic Ni (Scheme 3.17) [115]. However, there must be important differences between the reactions described by Eq. (3.19) and Scheme 3.17, since the former requires the addition of PMe_3, while the latter is inhibited by an excess of PEt_3.



(3.19)



Scheme 3.17.



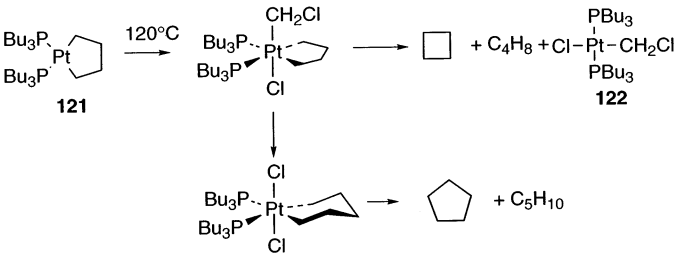
Scheme 3.18.

The reductive elimination of M(II) metalacycles can be efficiently induced by π-acceptor ligands such as maleic anhydride [19,54,112,146,147,180] as shown for example in Scheme 3.18 [146,147]. Interestingly, the reaction of the nickelacyclopentanes **120** with BF_3 gives the hydrocarbon **112** (Scheme 3.18), which is also produced by the pyrolysis of the palladium analog of **120** (see Eq. (3.16)). BF_3 alone does not induce the isomerization of pure **112** under the reaction conditions.

The effect of electron acceptor ligands may be understood on the basis of the destabilization of an hypothetical pentacoordinated species that results from the interaction with the metalacyclic complex due to partial electron-transfer from the metal to the ligand. In accord with this interpretation, the reductive elimination of Ni [19,112,180] or Pd [22] can be induced by oxidizing reagents such as molecular oxygen. Alkyl halides can also play a similar role, inducing the reductive elimination of pallada- and platinacycles. A closer look to the latter reaction, however, reveals that the species that decomposes is actually a Pd(IV) or Pt(IV) metalacycle, which will be examined in the following section.

3.2.2. Decomposition of M(IV) metalacycles

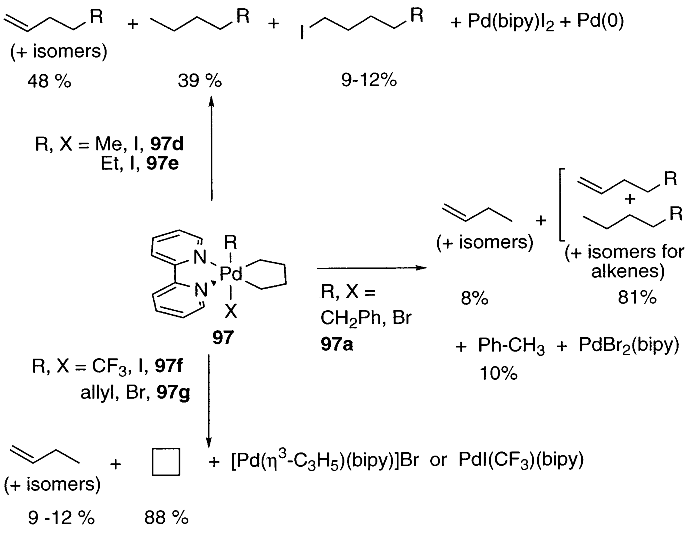
The reaction of alkyl halides and other electrophiles with metalacycles to form new M(IV) complexes was addressed in Section 3.1. The tendency of these compounds to decompose through a reductive elimination process is specially pronounced in the case of Pd, but can also be observed in Pt. In his pioneering studies on Pt metalacycles, Whitesides observed that, in dichlorometane the decomposition of platina(II)cyclopentane **121**, which contains the very basic PBu_3 ligands [207], produces mainly cyclobutane, together with butenes and other C_5 hydrocarbons (cyclopentane and pentenes), in contrast with the PPh_3 derivative, whose main decomposition products are butenes (Scheme 3.19). The decomposition of **121** in non-chlorinated solvents takes place normally, giving also butenes, and hence the different behavior of **121** in CH_2Cl_2 can be attributed to the oxidative addition of this solvent to the electron-rich Pt center, as evidenced by the identification of **122**



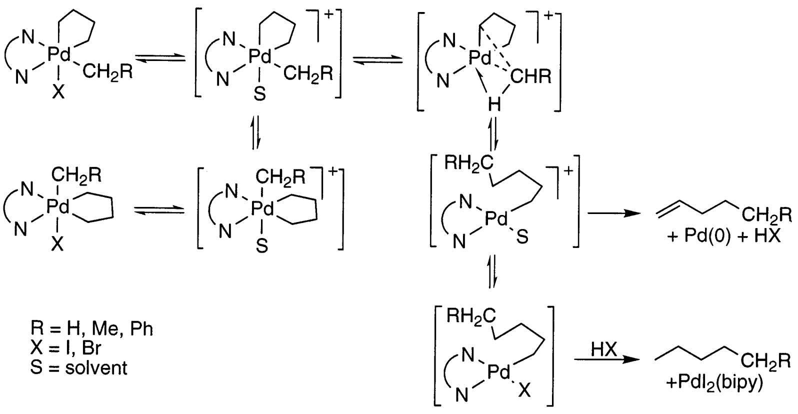
Scheme 3.19.

as the main organometallic product of the reaction (Scheme 3.19). The formation of C_5 hydrocarbons can be explained on the basis of a ring expansion to give a platina(IV)cyclopentane. This can then reductively eliminate cyclopentane or produce open-chain C_5 hydrocarbons thorough an undisclosed mechanism.

The decomposition of pallada(IV)cyclopentanes **97** (Scheme 3.20) has been recently studied by Canty [196]. It occurs readily at room temperature, and gives rise to different products depending on the nature of the R group attached to Pd. The *n* -alkyl derivatives (R = Me, Et), decompose yielding mainly products resulting from the coupling of the metalacycle and R units (a mixture of linear C_5 (R = Me) or C_6 (R = Et) alkanes and alkenes) while for R = CF_3 or allyl, this process does not take place, and the metalacyclic unit is eliminated as butene or cyclobutane. For R = benzyl, an intermediate situation was observed, and coupled products were formed together with butenes (Scheme 3.20). The ability of *n*-alkyl ligands to couple with the metalacyclic fragment has been explained in terms of the



Scheme 3.20.



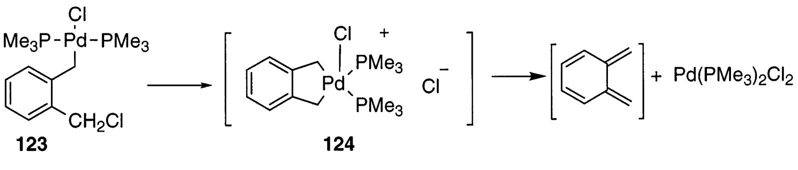
Scheme 3.21.

stabilization of the transition state of reductive elimination by an agostic interaction (Scheme 3.21). As shown also in Scheme 3.21, the formation of alkenes and alkanes from the derivatives with R = Me, Et or $PhCH_2$ can be accounted for on the basis of the decomposition of a Pd(II)-*n*-alkyl intermediate by β-elimination, previously investigated by Yamamoto [212,213]. On the other hand, deuteration experiments reveal that the formation of butene from the metalacycle unit when R benzyl, allyl or CF_3 is due to an intermolecular hydride-transfer chain similar to that proposed by Whitesides in his studies of the decomposition of platina(II)metalacycles.

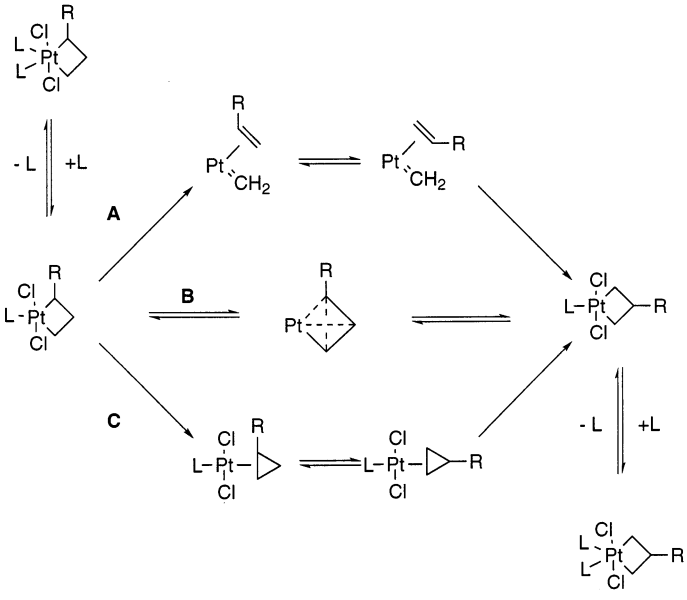
The palladium alkyl **123** undergo in solution an intramolecular oxidative addition process which is thought to lead to the Pd(IV) metalacycle **124**. The decomposition of this complex produces *o*-xylylene and therefore represents an unusual example of retro-cycloaddition from a Pd(IV) metalacycle (Scheme 3.22) [26].

A large volume of information is available concerning the decomposition and rearrangements of platina(IV)cyclobutanes. Although as mentioned on Section 2.3, the field has been reviewed recently [5,6,89] a brief account will be given here for the sake of comparison with other group-10 metalacycles of different size.

One of the most characteristic aspects of platina(IV)cyclobutane chemistry is the Puddephatt rearrangement, which explains the isomerization of substituted cyclobutane rings [6] (Cf. Scheme 3.13). Its mechanism remains uncertain despite the many efforts directed to its elucidation. Three possible pathways have been proposed (Scheme 3.23), of which B and C are fully consistent with the experimental data [214].



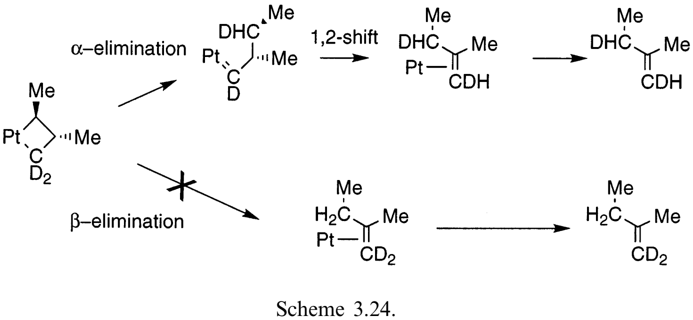
Scheme 3.22.



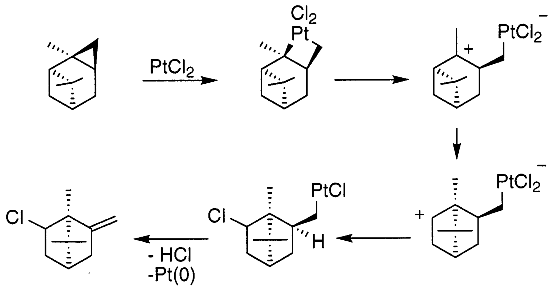
Scheme 3.23.

Even though the decomposition of platina(IV) cyclobutanes may involve β-H elimination, an investigation by Puddephatt of the decomposition of deuterium-labeled platina(IV)cyclobutanes has led to an isotopic distribution in the products which is consistent with an α-elimination process followed by a 1,2-hydrogen shift (Scheme 3.24) [215].

Sometimes, the decomposition of platina(IV)cyclobutanes is accompanied by a complex skeletal rearrangement that may be of interest in organic synthesis. Schemes 3.25 and 3.26 show some transformations which may be considered of 'carbenium-type' due to the carbocationic character of the carbon atom bonded to an electrophilic Pt(IV) center [216–219]. However a number of platina-(IV)cyclobutane decomposition reactions involve skeletal rearrangements which cannot be explained on this basis. Some of these transformations lead to ring



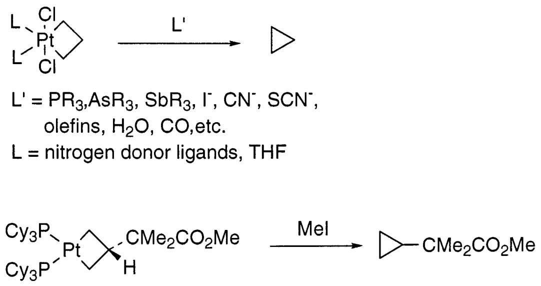
Scheme 3.24.



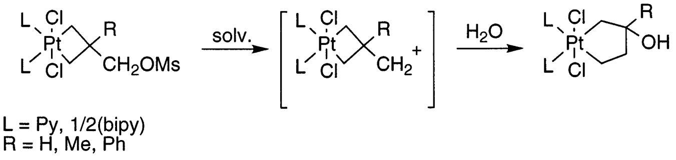
Scheme 3.25.

homologation and other useful organic transformations, such as those shown in Schemes 3.27 and 3.28 [220]. The reader is referred to Ref. [5] for a more complete account of this class of transformations.

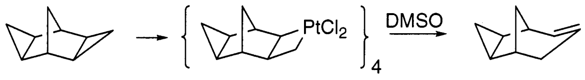
The presence of ligands with strong *trans* effect favors the reductive elimination of cyclopropane from platina(IV)cyclobutanes [5]. Thus, the addition of phoshines, arsines, stibines or anionic ligands (I^-, SCN^-, CN^-) to otherwise stable complexes induce their decomposition by reductive elimination (Eq. (3.20)). Olefins can also displace the metalacyclic moiety. The instability of the phosphine-based platinum complexes explains the reductive elimination shown in Eq. (3.21), which contrasts with the thermal decomposition of the same metalacycle that was presented in Eq. (3.14) [166].



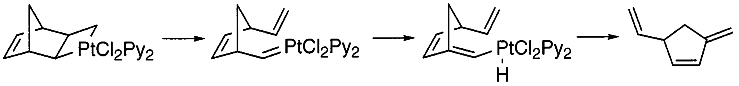
(3.20,3.21)



Scheme 3.26.



Scheme 3.27.



Scheme 3.28.

3.3. *Insertion reactions*

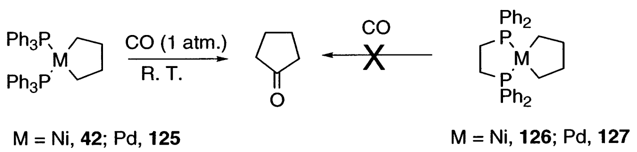
The reaction of group 10 metalacycles with small, unsaturated molecules may lead to their insertion into the M–C bonds and expansion of the ring. Often, a decomposition reaction (e.g. a reductive elimination) follows, yielding carbocyclic or heterocyclic organic products.

Although there might be some exceptions, the majority of the insertion reactions effected on Ni, Pd and Pt complexes can be regarded as 'migratory insertions' [1,221–223], i.e. reactions that involve the coordination of the unsaturated molecule to the metal, followed by an intramolecular attack of the alkyl ligand. The facility with which square-planar Ni(II) species incorporates a fifth ligand and the higher lability of the Ni compounds as compared with the analogous Pd(II) and Pt(II) complexes explain why insertion reactions are very common for nickelacycles but have only seldom been reported for the platinum analogs.

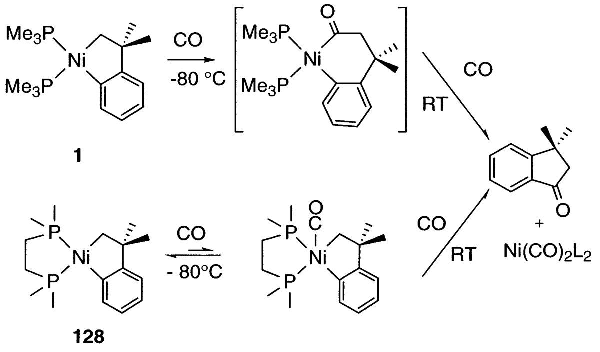
3.3.1. *Insertion of carbon monoxide and isocyanides*

The carbonylation of metalacycles allows their transformation to cyclic ketones. Therefore many reactions of this kind have been reported. In general, the insertion of one equivalent of CO is followed by the reductive elimination of a cyclic ketone, as shown in Scheme 3.29 for metalacyclopentanes of Ni, **42**, [19] and Pd, **125**, [21]. The reaction appears to be rather sensitive to the coligands present in the complex, and the corresponding derivatives of the chelating phosphine dppe, **126** and **127**, do not react with CO at 1 atm.

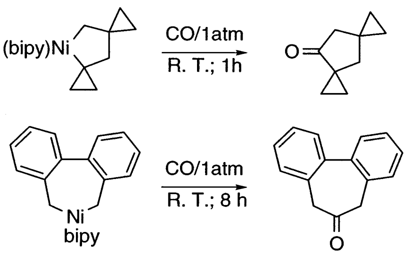
A similar effect has been noted for the metalacyclic system shown in Scheme 3.30. For the PMe_3 complex **1** the reaction is very fast even at low temperatures [11,12], while for the dmpe derivative **128** the 5-coordinate intermediate appears to exist in solution even at temperatures close to 0°C [224]. The bipy metalacycle does not react after 10 h of exposure to 2 atm of CO and therefore behaves similarly to the related $(bipy)\overline{NiCH_2CH_2CH_2CH_2}$ compound [180]. However, as shown in Eqs. (3.22) and (3.23), other metalacycles of Ni supported by bipy react readily with CO [54,129].



Scheme 3.29.

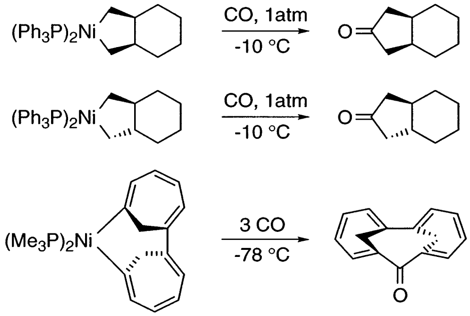


Scheme 3.30.

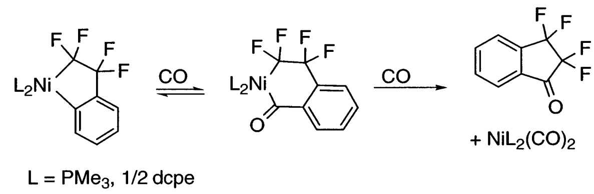


(3.22,3.23)

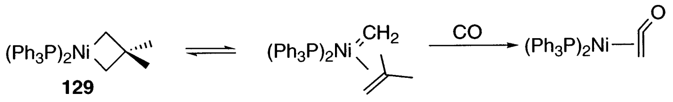
Scheme 3.31 [159] and Scheme 3.32 [70,225] and Eqs. (3.24) and (3.25) [117] and (3.26) [102] show representative reactions of carbonylation of nickelacyclic species. Other examples can be found in Refs. [27,128,130]. The reaction of Scheme 3.32 involves the nickelacyclobutane complex **129** and can be considered somewhat unusual since it affords a ketene complex instead of the expected cyclobutanone. As demonstrated by Grubbs and Miyashita (see also Section 3.2) the ketene ligand results from the coupling of CO with a Ni=CH_2 fragment [70,225].



(3.24,3.25,3.26)



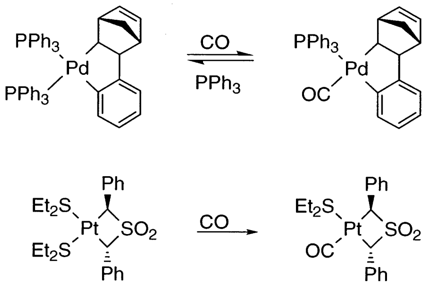
Scheme 3.31.



Scheme 3.32.

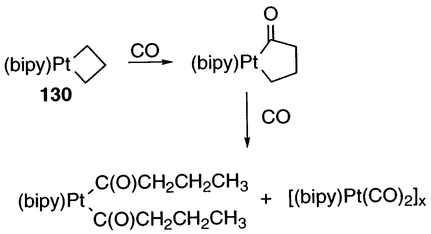
The reaction of the platinacyclobutane complex **130** with CO is also an unusual one. An isolable cyclic acyl forms initially but this rearranges with time to produce a bis(propionyl) complex of Pt(II) along with an ill-defined polymeric Pt(0) carbonyl (Scheme 3.33) [190].

The reactions of Schemes 3.29 and 3.33 constitute rare examples of insertion into the M–C bonds of Pd and Pt metalacycles. In other cases (Eqs. (3.27) and (3.28)) CO can displace a neutral ligand, giving rise [79,177] to square-planar metalacycles that contain CO in a *cis* position with respect to a M–C bond. The high kinetic barrier to insertion in these compounds may be associated with the restrictions imposed by the metalacycle for the migration of one of the CH_2 termini to the coordinated CO ligand, at variance with the facile situation encountered in the 5-coordinated Ni(II) intermediate [226].

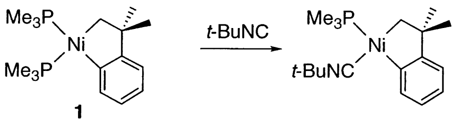


(3.27,3.28)

The reaction of isocyanides with metalacycles [11,37,80,177] usually leads to the formation of stable, square planar isocyanide adducts rather than to insertion products, even in the case of nickel. As shown in Eq. (3.29), *t*-BuNC displaces the PMe_3 ligand *trans* to the methylene group of **1**. This substitution pattern is due to the larger *trans* effect of the alkyl group as compared to the aryl, and has a profound influence in directing the regiochemistry of the insertion of alkynes, heterocumelenes and other substrates in this metalacycle [11]. The palladium analog of **1** displays the same behavior against *t*-BuNC [80].



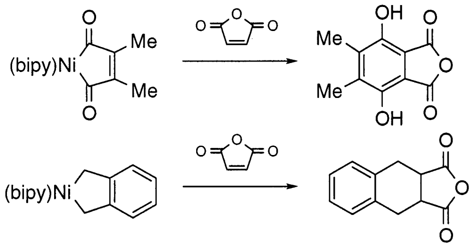
Scheme 3.33.



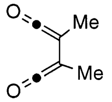
(3.29)

3.3.2. Insertion of alkenes, alkynes and allenes

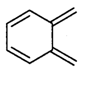
Although the insertion of alkenes into metalacycles of Pd occurs during certain catalytic processes (see Section 4.1), the stoichiometric reaction has been observed only rarely. Eqs. (3.30) and (3.31) depict two reactions [181,227] that might involve the insertion of maleic anhydride followed by reductive elimination. However, since maleic anhydride is known to induce reductive elimination, a more likely mechanism for these transformations would be the induced elimination (or retro-cycloaddition) of the diketene **131** and *o*-xylylene **132**, respectively, followed by a Diels–Alder condensation with maleic anhydride, as shown for the Pd (IV) metalacycle **124** (see Scheme 3.22).



(3.30,3.31)

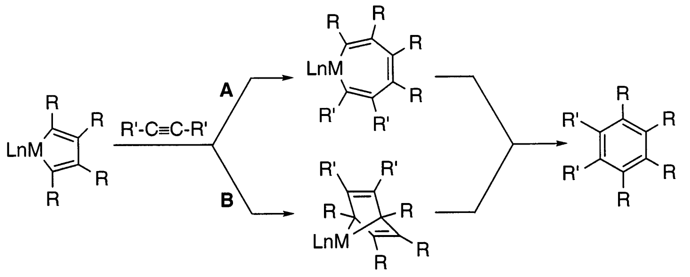


131

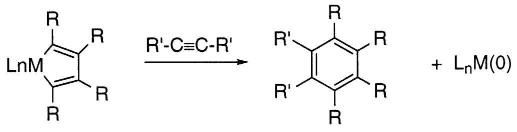


132

The reaction of alkynes with metalacycles is a well known process, which usually leads to the formation of organic carbocycles. Metalacyclopentadiene derivatives of Ni [27] and Pd [139,140] readily react with alkynes, giving rise to the formation of benzene rings (Eq. (3.32)). In the case of Pd, and when the alkyne is dmad, the reaction becomes catalytic. Scheme 3.34 shows the two mechanistic possibilities suggested for this reaction [4,228,229].

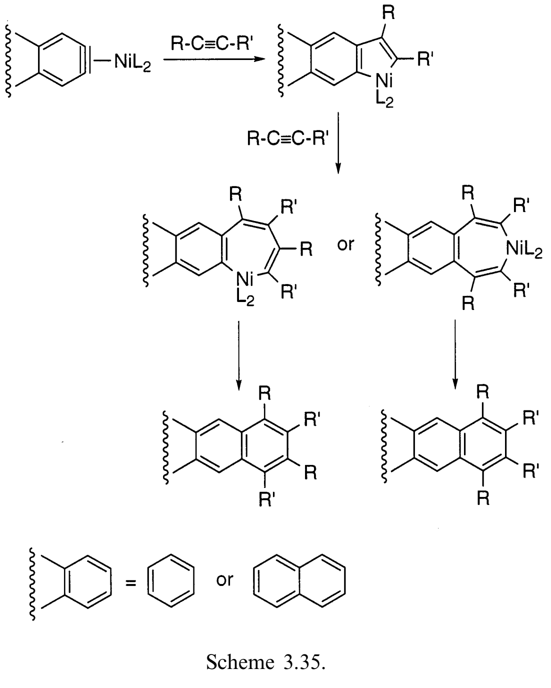


Scheme 3.34.

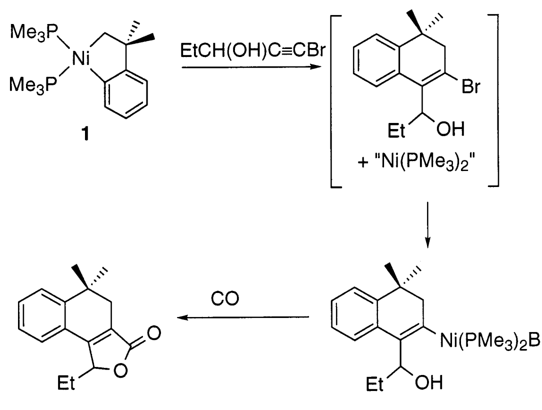


L_nM = (dppe)Ni; R = Ph; R' = H, Me, Ph, CO_2Me
L_nM = Pd; R = CO_2Me; R' Ph, CO_2Me (3.32)

The reaction of nickel benzyne or naphthalyne complexes with alkynes can give stable benzonickelacyclopentadienes (see Scheme 2.28), but in general these metalacycles can only be detected in favorable cases [157], since the reaction with a second equivalent of the alkyne is faster than the metalacycle formation (Scheme 3.35) [157,158,160]. The nature of the products suggests that the insertion of the second



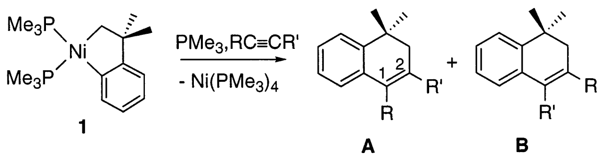
Scheme 3.35.



Scheme 3.36.

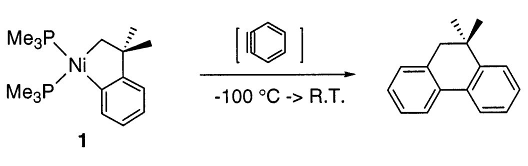
alkyne molecule may occur either at the M-aryl or the M-vinyl bond. The existence of two insertion points, coupled with the two possible orientations of the alkyne during the insertion makes difficult to predict the regiochemical outcome of this reaction.

The reactions of the benzaannelated nickelacyclopentene complex **1** with alkynes has been extensively studied by our group (Scheme 3.36 and Eqs. (3.33) and (3.34)) [11,12,230] including those of α- and β-bromoacetylenes. In the latter case the reductive elimination of the dihydronaphthalene is followed by the oxidative addition of the C–Br bond, giving new organometallic complexes that may undergo further transformations. The high efficiency of this insertion allows the trapping by **1** of unstable alkynes, such as benzyne (Eq. (3.34)).



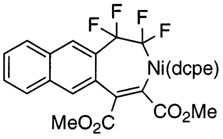
R	R'	A/B
H	H	
Ph	Ph	
p-C_6H_4Me	p-C_6H_4Me	
CO_2Me	CO_2Me	
H	CH_2CH_2OH	0.3
H	CH(OH)Et	1.6
H	Ph	1.8
H	*t*-Bu	2.2
Me	CH_2OH	3.0
H	CO_2Me	only **A**
Me	Ph	only **A**
Me	CO_2Me	only **A**
CH_2OH	Ph	only **A**

(3.33)



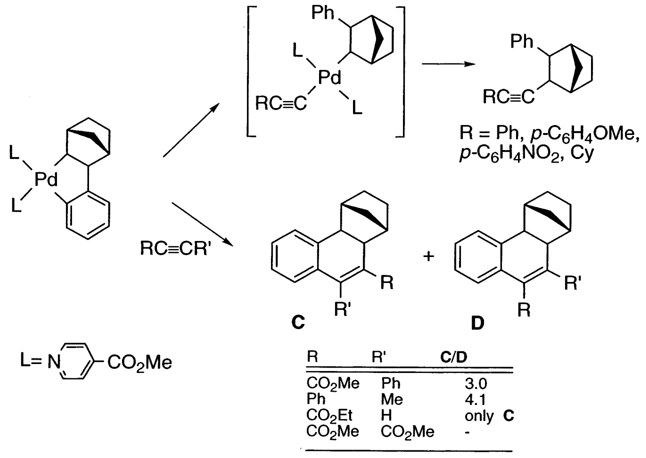
(3.34)

When the acetylene is unsymmetrically substituted, a mixture of the regioisomeric naphthalenes **A** and **B** is formed (Eq. (3.33)). At variance with other alkyne insertions into Ni-alkyl bonds [231–233], where the regioselectivity is controlled by steric factors, the electronic properties of the substituents of the alkyne have an important effect in their reaction with **1** and, thus, the higher selectivities are observed for the most polarized alkynes. The regioselectivity of the reaction favors the isomer with the most electronegative substituent in the 2 position, except for *t*-BuC≡CH, where the steric factors can overcome the electronic influence. In some cases seven-membered metalacycles like **133** have been isolated in the reactions of benzonickelacycles with alkynes [158,159] but in general these intermediates cannot be detected since they decompose readily to the corresponding organic products [159].



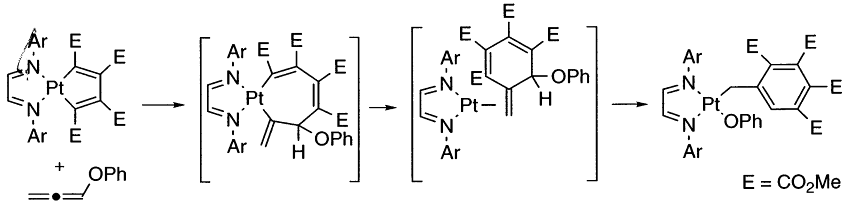
133

The scope of the reaction of palladacycles with alkynes is narrower than that of the nickel metalacycles, and is frequently limited to the activated acetylene dmad [36,37,79,80]. Catellani has found that the use of methyl isonicotinate coligands can expand the reactivity of palladacycles towards alkynes (Scheme 3.37). The resulting compounds **C** and **D** were in some cases accompanied by significant amounts of unidentified side products. The regioselectivity of the alkyne insertion is similar to that observed with the Ni complex **1**, and therefore an analogous insertion mechanism has been proposed. Interestingly, instead of inserting, terminal alkynes (with the exception of methyl propiolate) tend to react as weak acids and cleave, selectively the Pd–C bond. An example of this kind of reactivity had been previously noted by Cheng [79].



R	R'	C/D
CO$_2$Me	Ph	3.0
Ph	Me	4.1
CO$_2$Et	H	only **C**
CO$_2$Me	CO$_2$Me	-

Scheme 3.37.



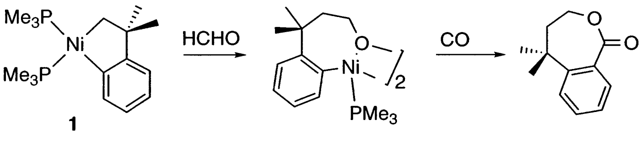
Scheme 3.38.

Although allenes are promising candidates to undergo insertion reactions, the reactivity towards group 10 metalacycles has been studied only sparsely. tom Dieck has devoted some attention to the investigation of catalytic transformations of allenes using palladium and platinum metalacycles, and has found that platinacyclopentadienes supported by diazabutadiene coligands react with allenes, as shown in Scheme 3.38 [127].

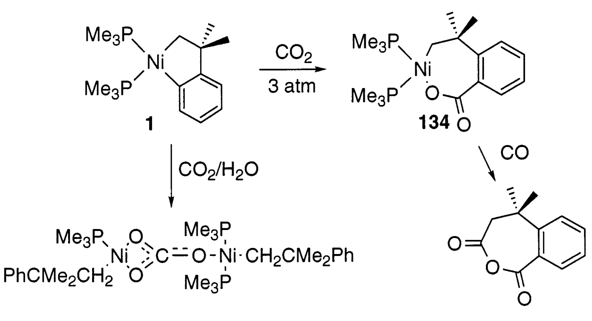
3.3.3. *Insertion of heteroalkenes and heterocumulenes*

The insertion of heteroalkenes (ketones, aldehydes, imines...) into nickel, palladium or platinum- carbon bonds is a rare type of reaction. However, the nickelacycle **1** reacts with formaldehyde, giving a cyclic binuclear alkoxide. This is the only case, with the possible exception of CO, in which the insertion takes place into the Ni–CH_2 bond of **1** [11,12]. The carbonylation of the alkoxide yields the corresponding lactone (Scheme 3.39).

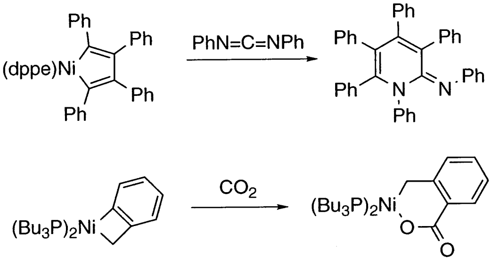
It is known from the pioneer work of Hoberg [234] that carbon dioxide, isocyanates and other related species readily undergo cocyclization and cooligomerization reactions with other unsaturated molecules mediated by nickel (0) complexes. However, despite its potential interest in heterocyclic synthesis, the reactivity of group 10 metalacycles, specially of nickel, towards heterocumulenes of type X=C=Y (where X, Y = O, S, NR) has received little attention, perhaps with the exception of the nickelacycle **1**, whose reactivity towards heterocumules has been thoroughly studied [11,12,230,235,236]. Before this, it was known that nickel metalacycles can undergo the insertion of carbodiimides [27] (Eq. (3.35)) and CO_2 [101] (Eq. (3.36)).



Scheme 3.39.



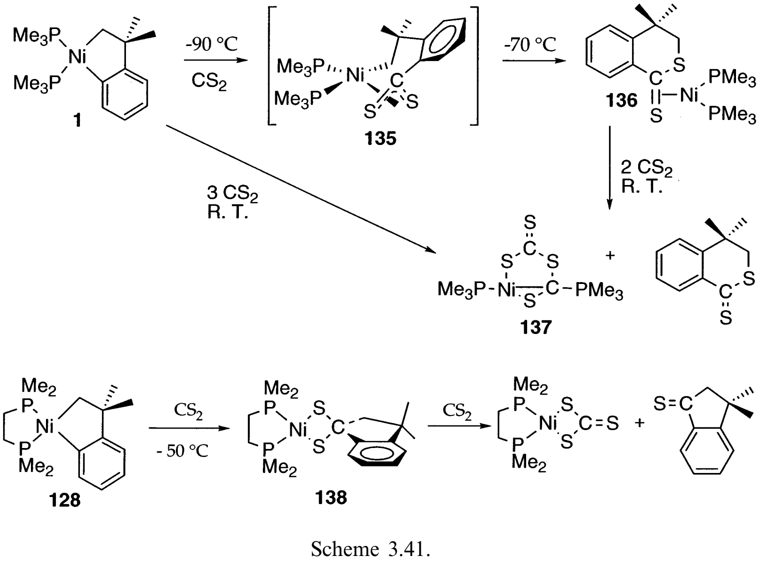
Scheme 3.40.



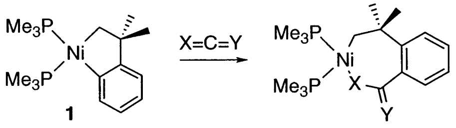
(3.35,3.36)

The nickelacycle **1** reacts slowly with dry CO_2 giving [11,12] the nickelalactone **134** which can be converted into a cyclic anhydride by reaction with CO (Scheme 3.40). In the presence of traces of water, a binuclear carbonate complex is instead obtained.

The reaction of **1** with CS_2 is much faster, and proceeds at −90°C to give an intermediate η^3-dithiocarboxylate, **135** which rearranges above −70°C to the



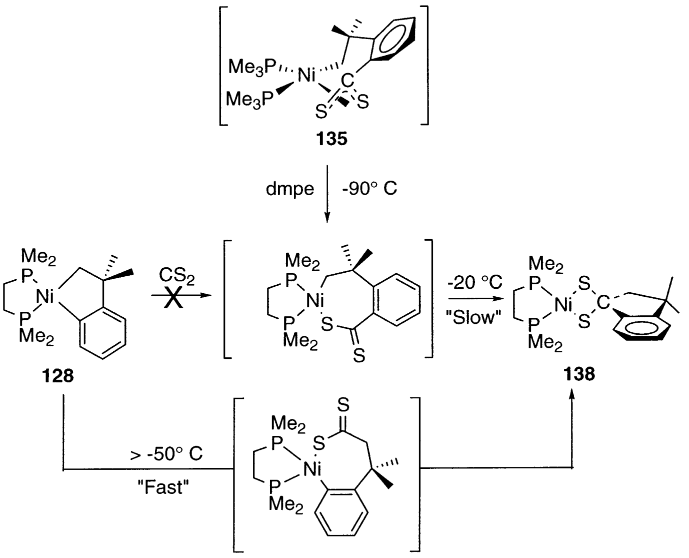
Scheme 3.41.



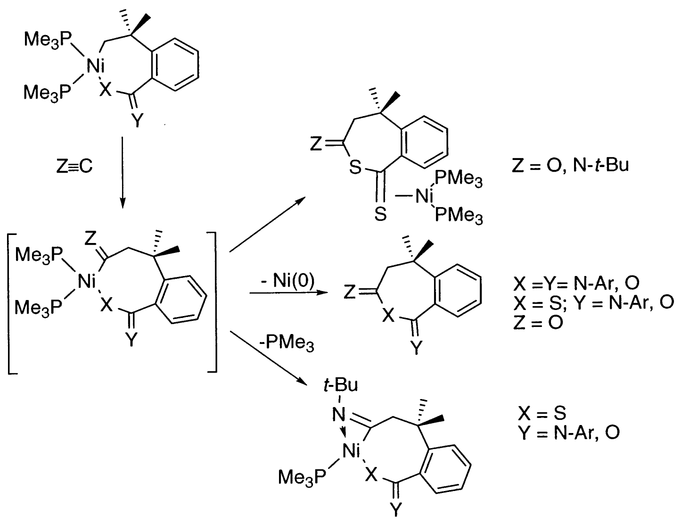
X, Y = S, S (CS_2); S, O (COS), S, NPh (PhNCS);
NPh, O (PhNCO); N-*p*-tolyl, N-*p*-tolyl, (C(N-*p*-tolyl)$_2$)
O, O (CO_2) (3.37)

thermally stable η^2-dithiolactone complex **136** [224,235]. This compound can react with an excess of CS_2 at room temperature, releasing the dithiolactone ligand, and producing the sulfur ylide complex **137**, which was previously known to form from Ni(0) complexes and CS_2 [237]. (Scheme 3.41). These products are also formed in high yield when **1** is reacted with an excess of CS_2 at room temperature. Rather unexpectedly, the dmpe-containing metalacycle **128** reacts with CS_2 in a different fashion, affording the 1,1-dithiolate **138**, without any detectable intermediates (Scheme 3.41). In the presence of an excess of CS_2, the dithiolate **138** reacts further and forms a trithiocarbonate complex and a cyclic thioketone. Thus, the overall reaction of the nickel metalacycle with two equivalents of CS_2 represents an unusual example of the disproportionation of the heterocumulene into trithiocarbonate and thiocarbonyl, the latter becoming incorporated into the thioketone functionality.

The reaction of other heterocumulenes with **1** takes place analogously to that of CO_2, with selective insertion into the Ni-aryl bond, as described in Eq. (3.37). The facility of the insertion of the C=X unit into the Ni–aryl bond follows the sequence C=S > C=N > C=O.



Scheme 3.42.



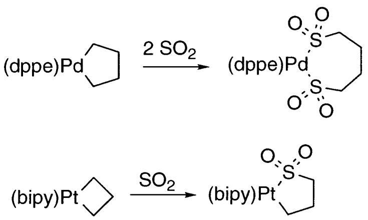
Scheme 3.43.

An interesting point in connection with the reactivity of CS_2 is whether its insertion in the dmpe derivative takes also place initially into the Ni–aryl bond. Competition experiments using both the PMe_3 and the dmpe metalacycles (Scheme 3.42) show that in the latter case CS_2 inserts into the Ni–CH_2 bond.

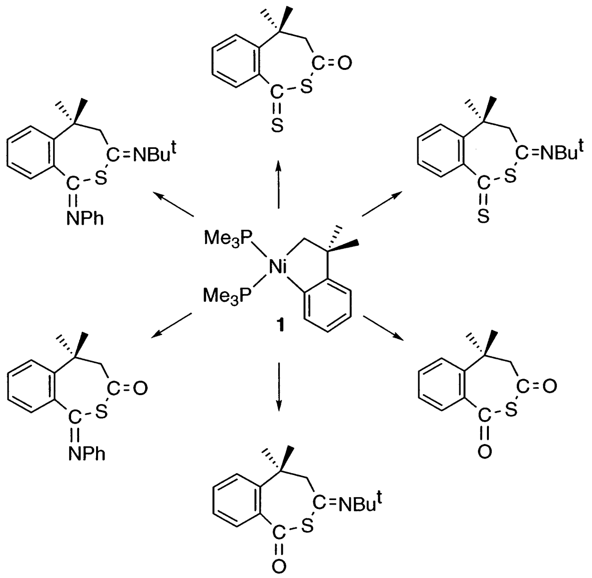
The products resulting from the reaction of **1** with heterocumulenes still contain an intact Ni–C bond which readily undergoes the additional insertion of CO and isocyanides. This reaction provides direct access to cyclic, seven-membered anhydride derivatives, although in other cases isolable complexes are formed which require further chemical manipulation in order to release the corresponding organic molecule (Scheme 3.43) [235,236]. An special case is the product resulting from the successive insertion of CS_2 and CO which is also formed when **1** is reacted with CO first, and then with CS_2. Since CS_2 inserts into the Ni–aryl bond, this observation suggests that CO inserts into the Ni–CH_2 functionality of **1**, (see Scheme 3.30) [236]. Scheme 3.44 summarizes the organic products resulting from the sequential incorporation of heterocumulenes and CO or isocyanides into the Ni–C bonds of **1**.

3.3.4. Insertions of SO_2, O, S, Se and Te

Sulfur dioxide has been reported to insert into the M–C bonds of pallada- and platina-cycloalkanes to give *S*-sulfinates. As shown in Eqs. (3.38) [21,238] and (3.39) [190] the insertion can take place in one or in both M–C bonds.



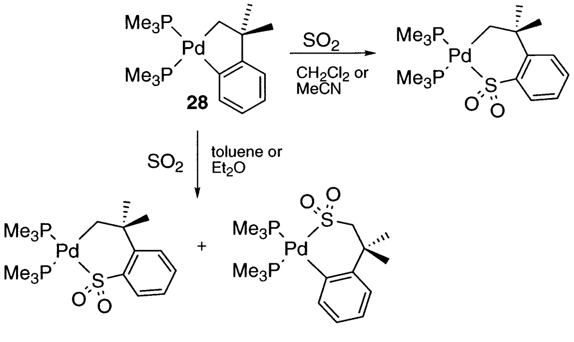
(3.38,3.39)



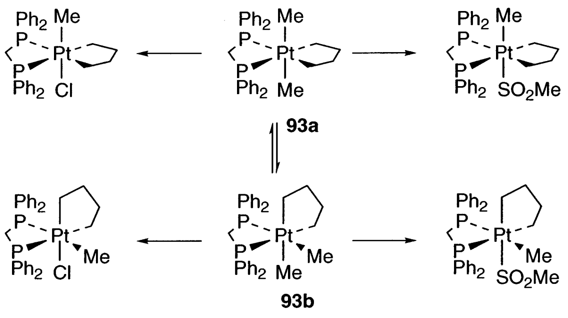
Scheme 3.44.

The reaction of **28**, i.e. the Pd analog of **1**, with SO_2 gives only monoinserted products. However, the regioselectivity of the insertion depends on the solvent used for the reaction. In polar solvents (acetonitrile, dichloromethane), the insertion occurs selectively at the Pd–carbon bond, while in less polar solvents, such as toluene or diethyl ether, a mixture of regioisomers is obtained, suggesting that two different insertion mechanisms can operate (Scheme 3.45) [80].

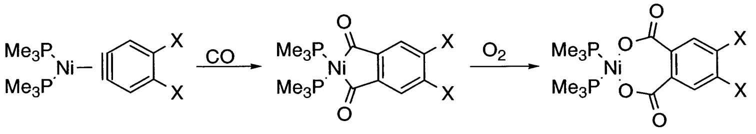
The reaction of sulfur dioxide with organometallic compounds is considered to proceed more as a direct electrophilic attack to the metal-bound carbon atom than as a migratory insertion [239,240]. In accord with this behavior, the reaction of the Pt(IV) metalacyclopentanes **93a** and **93b** with SO_2 resembles their protonolysis with HCl, cleaving the terminal Pt–CH_3 rather than the Pd–CH_2 bond (Scheme 3.46) [241].



Scheme 3.45.



Scheme 3.46.

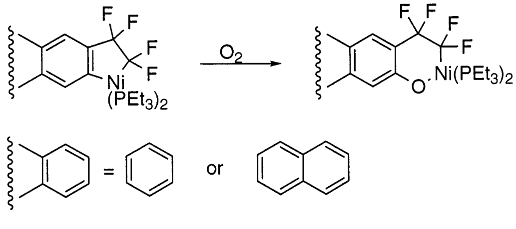


Scheme 3.47.

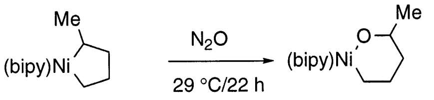
Molecular oxygen is a strong oxidizing reagent that often causes the decomposition of organometallic compounds. Whereas in some cases the reaction of metalacycles with oxygen may lead to complex mixtures [115], in others, oxygen can react selectively resulting in the insertion of an oxygen atom. An interesting case is shown on Scheme 3.47 [164] where the unstable bis(acyl)metalacyclic species that results from the reaction of nickel-benzyne complexes with a large excess of CO reacts with O_2 to give nickel ftalate complexes. Hoberg has applied this reactivity to the synthesis of cyclic acid anhydrides [112].

Eq. (3.40) shows some examples of a selective insertion of an oxygen into the Ni–aryl bond of the fluorinated metalacycles [159].

Hillhouse has investigated the use of dinitrogen monoxide (N_2O) as an oxygen transfer agent. Its reaction with some nickelacyclopentane derivatives [181,182,242] leads to the insertion of a single oxygen atom. Eq. (3.41) is a representative example of this kind of reaction. He has also shown that the interaction of N_2O with the nickelacycle **1** leads regioselectively to the product of insertion into the Ni–aryl bond [243].

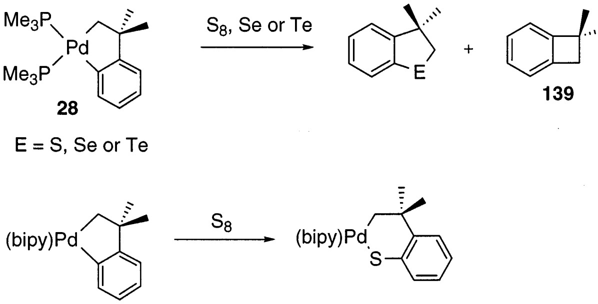


(3.40)



(3.41)

The palladium metalacycle **28** does not react with O_2, but it does with S_8, giving 3,3-dimethyldihydrobenzothiophene, together with smaller amounts of the benzocyclobutene **139** resulting from the reductive elimination of the metalacycle (Eq. (3.42)) [80]. When the phosphine ligands of **28** are replaced by bipy, it is possible to isolate an intermediate complex that contains the sulfur atom inserted into the Pd–aryl bond (Eq. (3.43)). The Se and Te analogs could be also obtained by reacting **28** with elemental Se and Te (Eq. (3.42)), but in the case of Te, much better results were obtained with trimethylphosphine telluride [80]. Other similar reactions like those with N_2O, CO_2, CS_2, COS and related molecules are presently being investigated.



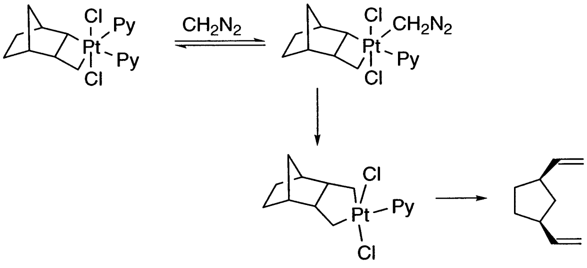
(3.42,3.43)

3.3.5. Carbene insertion reactions

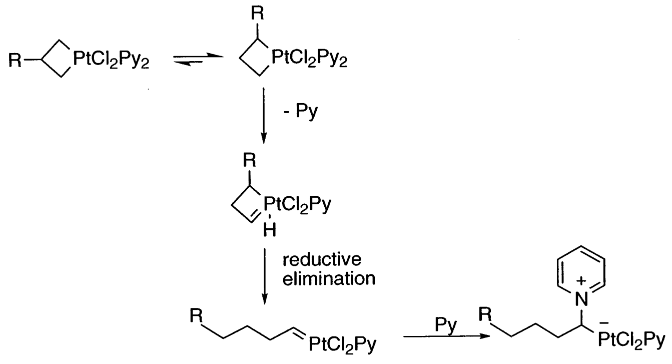
The reaction of platina(IV)cyclobutanes with diazomethane can lead to the formation of organic products that incorporate a new methylene unit [244–246]. The mechanism of this reaction involves the coordination of diazomethane to platinum, followed by ring expansion and elimination of the organic fragment by a retro-cycloaddition reaction (Scheme 3.48).

3.4. Reactions yielding carbene and ylide complexes

It was mentioned in Section 3.1 that fluorine abstraction by BF_3 from perfluoronickelacyclopentane complexes affords ylide type derivatives (Scheme 3.11), presumably *via* highly electrophilic nickel carbene intermediates.



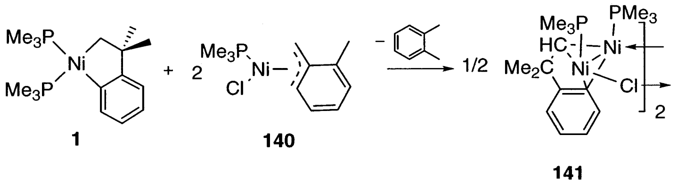
Scheme 3.48.



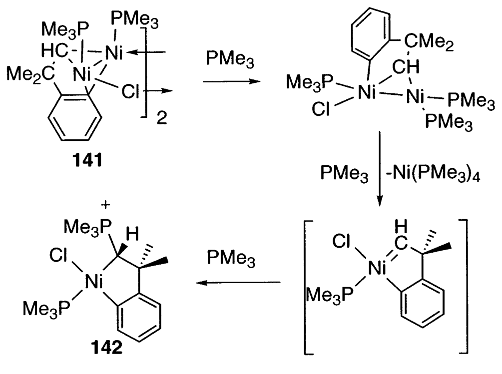
Scheme 3.49.

Platina(IV)cyclobutanes can undergo spontaneous rearrangement to ylide complexes [247–251] as shown in Scheme 3.49, this transformation is proposed to involve an α-elimination reaction to give a carbene ligand, which is then stabilized as the pyridinium ylide [250].

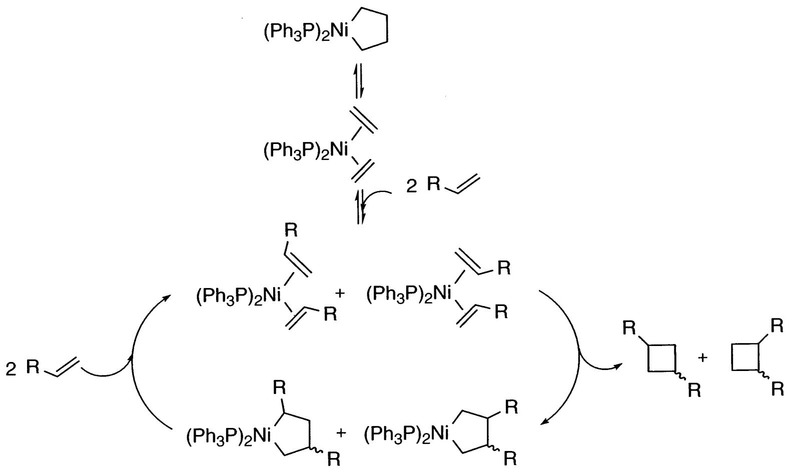
The interaction of the nickelacycle **1** with the η^3-xylyl complex **140** provides an unusual example of intermolecular α-H abstraction. An alkylidene-bridged binuclear species **141** and *o*-xylene are produced [252,253] in this reaction (Eq. (3.44)). A similar transformation takes place between **1** and Ni(η^5-Cp)(η^3-C_3H_5). Attempts to prepare a mononuclear nickel alkylidene complex led to the ylide **142**, presumably through the intermediacy of the desired alkylidene, as shown in Scheme 3.50 [254].



(3.44)



Scheme 3.50.



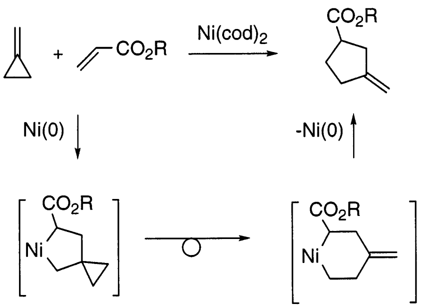
Scheme 4.1.

4. Group 10 metalacycles as reactive intermediates in catalysis

Metalacyclic complexes of Ni and Pd are involved as intermediates in many different catalytic or stoichiometric transformations of synthetic or even technological interest [7–10,120,121]. Many of these processes can now be understood in light of the stoichiometric reactions that have been discussed in Sections 2 and 3. The comprehensive description of every synthetic application that can possibly involve the latter species is much beyond the aims and scope of this review, but an overview of some representative examples in which their participation is well-established is necessary in order to give a complete picture of the chemistry of this class of compounds. To this end, we will examine first processes in which the oxidation state of the metal varies between 0 and II, then those that involves the II/IV oxidation change, and finally some examples in which the metal center goes through the states 0, II and IV.

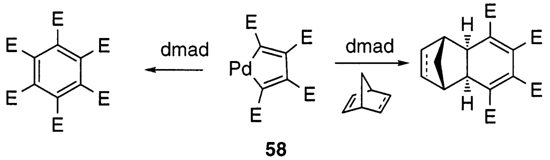
4.1. Processes involving the 0/II oxidation states

Some olefin 2 + 2 dimerization reactions catalyzed by nickel, developed by Grubbs [255] are among the simplest of these processes. This reaction involves the oxidative coupling of the two olefin fragments by Ni(0), followed by the decomposition of the nickelacyclopentane complex by reductive elimination (Scheme 4.1). A slightly different reaction gives cyclopentanes from methylenecyclopropane derivatives and acrylates (Scheme 4.2) [256].

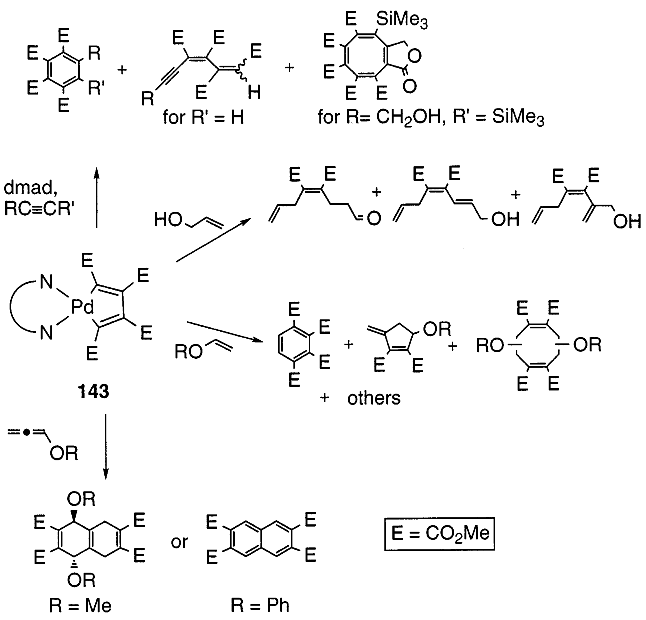


Scheme 4.2.

The oligomerization of alkynes catalyzed by nickel and palladium complexes is a well known process. As already discussed in Section 2.4, palladium (0) complexes catalyze the cyclotrimerization of dmad [139,140,257,258]. The resting state of the catalyst is the palladacyclopentadiene **58** (see Scheme 2.23). This catalytic system can also cotrimerize dmad and alkenes [143a,259] to give dihydrobenzenes (Scheme 4.3). tomDieck has studied this catalyst modified by diazabutadiene ligands, **143**, and has systematically developed its application to the cotrimerization of dmad with alkynes [144a,260], alkenes [163,261], and allenes [127,162]. As shown in Scheme 4.4, the outcome of these reactions can be quite complex, and mixtures of different types of products can be obtained. Thus, the substituted benzenes resulting from the cocyclotrimerization of dmad with terminal alkynes are accompanied by minor amounts of open-chain alkynes. This clearly indicates that the alkyne can act as a weak acid, cleaving a Pd–C bond of **143** [144a]. The production of cyclooctatetraenes, suggests a multiple alkyne insertion into **143** [260]. Although **143** is not able to catalyze the cooligomerization of dmad with unactivated alkenes, a catalytic reaction ensues with allyl alcohol or vinylic ethers or esters, giving diverse cyclic or alicyclic products. The formation of these products can be explained assuming that the intermediate palladacyclopentene inserts a second molecule of the alkene to give a palladacycloheptene, which then evolves through different reaction pathways. The reaction of dmad and alkoxyallenes is a remarkable one, giving naphtalene derivatives. The mechanism of this reaction is complex [162] and probably involves the Diels–Alder reaction of dmad with intermediate palladacycles similar to the Ni and Pt complexes **51**–**54** (Section 2.4.1.1), which are formed by interaction of allenes with M(0) species, as previously discussed.

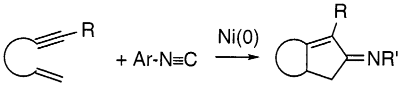


Scheme 4.3.

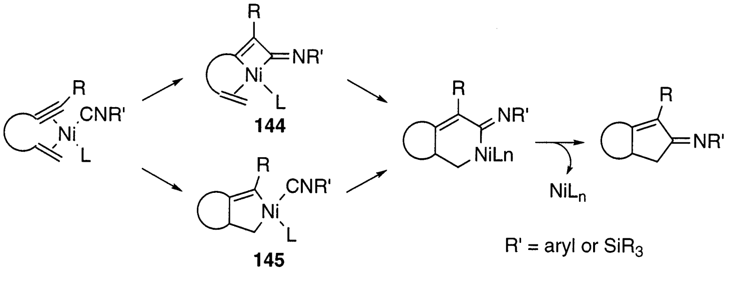


Scheme 4.4.

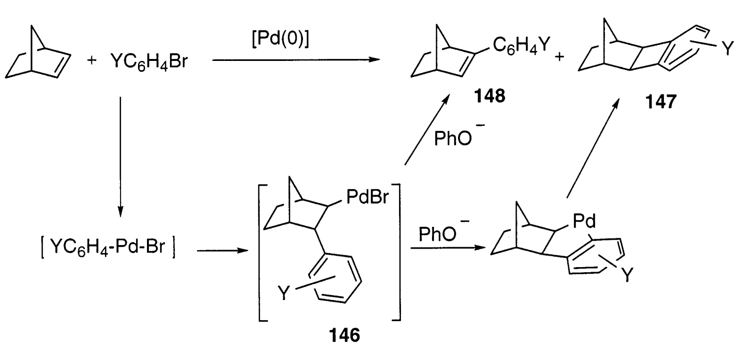
Another interesting cyclization process, induced in this case by Ni, is the Pauson–Khand reaction of enynes with isocyanides, which gives cyclopentenone imines (Eq. (4.1)) [262,263]. Due to the formation of very stable and unreactive Ni(0) isocyanide complexes, the reaction is stoichiometric with aryl isocyanides, but it becomes catalytic when these are replaced by trialkylsilyl isocyanides [264]. Two possible mechanisms, involving the intermediate metalacycles **144** and **145** are possible (Scheme 4.5) but, on the basis of the observed side products, the authors prefer the first one.



(4.1)



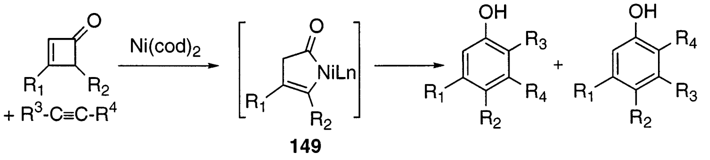
Scheme 4.5.



Scheme 4.6.

The formation of intermediate palladacycles by cyclometalation reactions is responsible for a number of palladium-catalyzed cyclizations used in organic synthesis [8]. Some of these reactions can be rather complex, and imply palladium species in the 0, II and IV oxidation states. Of special interest are those developed by Catellani and Chiusoli, shown in Scheme 4.6 [7,265,266]. The mechanism of this reaction, insertion of norbornene into a Pd-aryl bond, followed by a cyclometalation reaction, became clear after the isolation and characterization of the intermediate metalacycles **146**, stabilized by different ligands (see Scheme 2.9). The otherwise unstable species decompose by reductive elimination giving the corresponding cyclobutanes, **147**. A byproduct of this reaction is the (formally) Heck-type compound **148**, which results from the β-hydrogen abstraction by the base (KOPh). The formation of **148** can be avoided using bulkier phenolates. Other examples of Pd-catalyzed cyclization reactions with similar mechanisms can be found in Refs. [7,8].

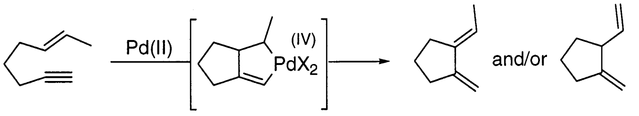
In the nickel catalyzed synthesis of substituted phenols shown in Eq. (4.2), the catalytic species is generated by oxidative addition of a cyclobutenone to a Ni(0) center [267]. The nickelacyclobutenone complex **149** appears a likely intermediate



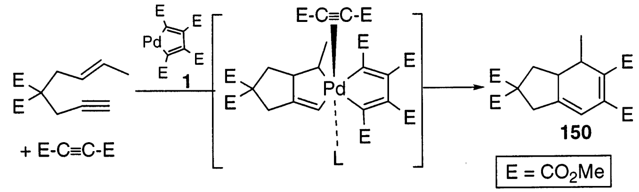
(4.2)

4.2. Processes involving the II/IV oxidation states

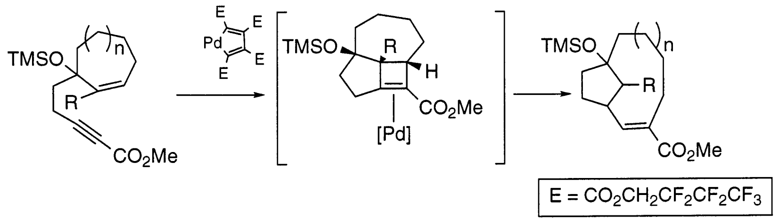
The palladium (II) catalyzed intramolecular Alder's *ene* reaction of enynes, described by Trost, is one example of this type of process (Eq. (4.3)) [268,269]. The initially used palladium acetate is advantageously replaced by the Pd(II) metalacycle **58**, activated by the addition of a coligand such as tris(*o*-tolyl)phosphite. In this case it is possible to trap the intermediate Pd(IV) metalacycle with dmad, and the reaction leads to the [2 + 2 + 2] cycloadduct **150** (Eq. (4.4)) [270]. This dmad insertion is a rare example of reactivity that has not been observed yet on well characterized Pd(IV) metalacycles. In some instances, this reaction leads to the formation of rearranged products (Scheme 4.7). Different mechanistic possibilities may be envisaged for the formation of these compounds [271–273]. The transformation, which has been termed 'enyne methatesis reaction', can be promoted more efficiently by replacing the methoxycarbonyl groups of **58** by more electron-withdrawing substituents, such as fluorinated alkoxycarbonyl groups, allowing the high-yield synthesis of bridged bicycles with bridgehead olefins, as shown In Eq. (4.5) [274].



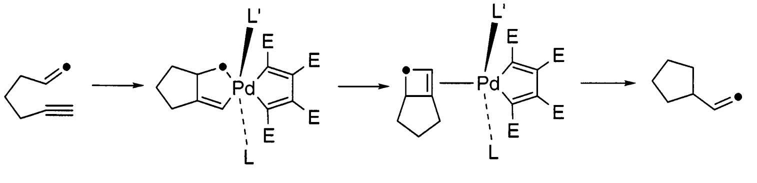
(4.3)



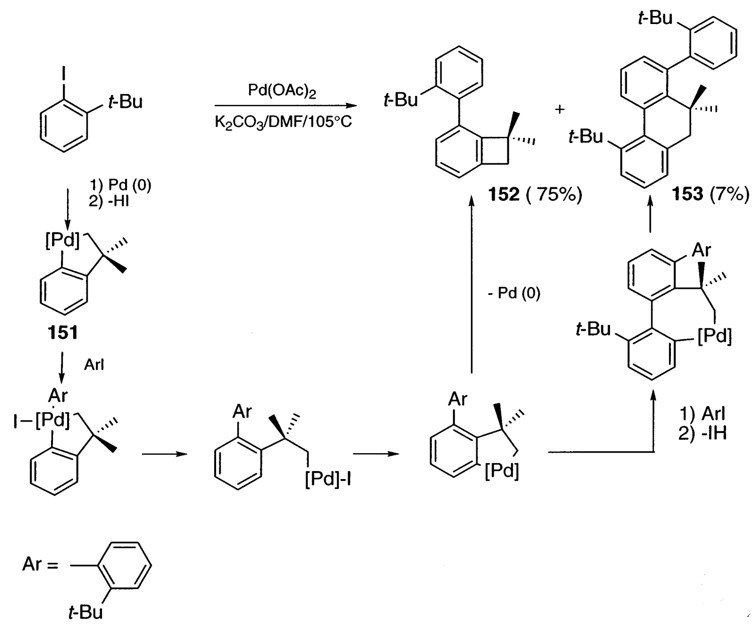
(4.4)



(4.5)



Scheme 4.7.

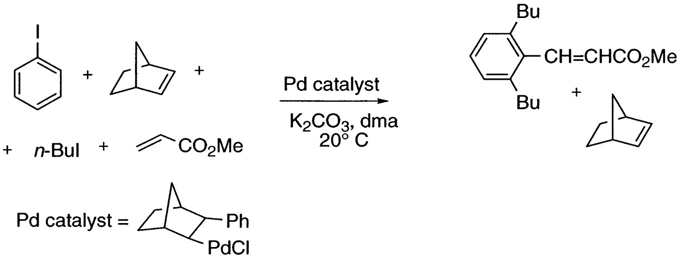


Scheme 4.8.

4.3. Processes involving the 0/II/IV oxidation states

Dyker [8], Catellani [7,275] and de Meijere [276,277] have described a set of cyclooligomerization reactions of substituted aryl halides whose mechanism apparently involves successive oxidative addition of aryl halide to Pd(0), cyclometalation and a second oxidative addition of aryl halide, this time to Pd(II), which fits into the scheme of this section. A good example of this reaction is depicted in Scheme 4.8 [278]. Interestingly, the first metalacyclic intermediate, **151**, has been prepared in the form of the adduct of different ligands (see Scheme 2.11) by activation of an aryl C–H bond of a neophyl ligand, although the aliphatic C–H activation reaction has also proven possible [81]. In the example of Scheme 4.8, the main product is **152**, resulting from the reductive elimination of the second metalacyclic intermediate. However, minor amounts of the product **153** are also produced, indicating that the whole process can be repeated for a second time. This is the more frequent outcome in other related reactions [8].

A drawback of the mechanism represented in Scheme 4.8 is the proposed oxidative addition of aryl halides to Pd(II), a kind of reactivity which has not been observed in reactions of isolated Pd(II) complexes. Although this type of oxidative addition could occur under the catalysis conditions, an alternative explanation is the intermolecular transfer of the aryl group from other Pd(II) aryl species, as proposed by Yamamoto [279,280]. The multicomponent catalytic transformation depicted by Eq. (4.6) almost certainly involves a true oxidative addition of alkyl halide to an intermediate palladacyclopentane [281]. The mechanism of this reaction, which was discussed in Scheme 3.1 (see Scheme 3.6), also implies a β-C–C cleavage, and therefore there is no net incorporation of norbornene.



(4.6)

References

[1] J.P. Collman, L.S. Hegedus, L.S. Norton, R.G. Finke, Principles and Applications of Organometallic Chemistry, University Science Books, Mill Valey CA, 1987.
[2] (a) S.D. Chappell, D.J. Cole-Hamilton, Polyhedron 1 (1982) 739. (b) E. Lindner, Adv. Heterocyclic Chem. 39 (1986) 237.
[3] (a) A.K. Smith, in E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), R.J. Puddephatt (Vol. Ed.), Comprehensive Organometallic Chemistry II, Vol. 9, Pergamon, Oxford. 1995, p. 29. (b) A.J. Canty, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), R.J. Puddephatt (Vol. ed), Comprehensive Organometallic Chemistry II, Vol 9, Pergamon, Oxford 1995, p. 225. (c) G.K. Anderson, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), R.J. Puddephatt (Vol. Ed.), Comprehensive Organometallic Chemistry II, Vol 9, Pergamon, Oxford 1995, p. 431.
[4] G. Ingrosso, in: P.S. Braterman (Ed.), Reactions of Coordinated Ligands, Plenum Press, New York, 1986, p. 639.
[5] P.W. Jennings, L.L. Johnson, Chem. Rev. 94 (1994) 2241.
[6] R.J. Puddephatt, Coord. Chem. Rev. 33 (1980) 149.
[7] M. Catellani, G.P. Chiusoli, Gazz. Chim. Ital. 123 (1993) 1.
[8] G. Dyker, Chem. Ber. 130 (1997) 1567.
[9] J. Eisch, A.A. Aradi, M.A. Lucarelli, Y. Quian, Tetrahedron 58 (1998) 1169.
[10] I. Ojima, M. Tzmarioudaki, Z. Li, R. Donovan, Chem. Rev. 96 (1996) 635.
[11] E. Carmona, P. Palma, M. Paneque, M.L. Poveda, E. Gutiérrez-Puebla, A. Monge, J. Am. Chem. Soc. 108 (1986) 6424.
[12] E. Carmona, E. Gutiérrez-Puebla, J.M. Marín, A. Monge, M. Paneque, M.L. Poveda, C. Ruiz, J. Am. Chem. Soc. 111 (1989) 2883.
[13] E. Carmona, J. Cámpora, M.A. Muñoz, M. Paneque, M.L. Poveda, Pure Appl. Chem. 61 (1989) 1701.
[14] J. Cámpora, M. Paneque, M.L. Poveda, E. Carmona, Synlett, (1994) 465.
[15] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 95 (1973) 4452.
[16] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.
[17] R.H. Grubbs, A. Miyashita, M.I. Liu, P.L. Burk, J. Am. Chem. Soc. 99 (1977) 3863.
[18] R.H. Grubbs, A. Miyashita, J. Am. Chem. Soc. 100 (1978) 1300.
[19] R.H. Grubbs, A. Miyashita, M. Liu, P. Burk, J. Am. Chem. Soc. 100 (1978) 2418.
[20] P. Diversi, G. Ingrosso, A. Lucherini, J. Chem. Soc. Chem. Commun. (1978) 735.
[21] P. Diversi, G. Ingrosso, A. Lucherini, S. Murtas, J. Chem. Soc. Dalton Trans. (1980) 1633.
[22] P. Diversi, G. Ingrosso, A. Lucherini, T. Lumini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1988) 133.

[23] G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.

[24] M.F. Lappert, T.R. Martin, C.L. Raston, Inorg. Synth. 26 (1989) 144.

[25] M.F. Lappert, T.R. Martin, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1982) 1959.

[26] J. Cámpora, C. Graiff, P. Palma, E. Carmona, A. Tiripicchio, Inorg. Chim. Acta 269 (1998) 191.

[27] H. Hoberg, W. Ricuter, J. Organomet. Chem. 195 (1980) 355.

[28] J.J. Eisch, J.E. Galle, J. Organomet. Chem. 96 (1975) C23.

[29] J.J. Eisch, A.M. Piotrowski, A.A. Aradi, C. Krüger, M.J. Romão, Z. Naturforsch Teil B 40 (1985) 624.

[30] C. Lawrie, K.P. Gable, B.K. Carpenter, Organometallics 8 (1989) 2274.

[31] S.A. Gardner, H.B. Gordon, M.D. Raush, J. Organomet. Chem. 60 (1973) 179.

[32] R. Usón, J. Vicente, J.A. Cirac, M.T. Chicote, J. Organomet. Chem. 198 (1980) 105.

[33] H.A. Brune, R. Hohenadel, G. Schmidtberg, U. Ziegler, J. Organomet. Chem. 402 (1991) 179.

[34] T. Debaerdemaeker, R. Hohenadel, H.A. Brune, J. Organomet. Chem. 410 (1991) 265.

[35] T. Debaerdemaeker, R. Hohenadel, H.A. Brune, J. Organomet. Chem. 350 (1988) 109.

[36] D.J. Cárdenas, C. Mateo, A.M. Echevarren, Ang. Chem. Int. Ed. Engl. 33 (1994) 2445.

[37] C. Mateo, D.J. Cárdenas, C. Fernández-Rivas, A.M. Echevarren, Chem. Eur. J. 2 (1996) 1996.

[38] C. Mateo, C. Fernández-Rivas, D.J. Cárdenas, A.M. Echevarren, Organometallics 17 (1998) 3661.

[39] H.O. Fröhlich, B. Hilper, B. Hofmann, J. Organomet. Chem. 430 (1992) 133.

[40] R. Wyrwa, H.O. Frölich, H. Görls, J. Organomet. Chem. 491 (1995) 41.

[41] H.O. Fröhlich, R. Wyrwa, H. Görls, J. Organomet. Chem. 456 (1993) 7.

[42] H.O. Fröhlich, R. Wyrwa, H. Görls, U. Pieper, J. Organomet. Chem. 471 (1994) 23.

[43] R. Wyrwa, H.O. Fröhlich, H. Görls, J. Organomet. Chem. 503 (1995) 135.

[44] H.O. Fröhlich, R. Wyrwa, H. Görls, Ang. Chem. 105 (1993) 425.

[45] H.A. Brune, H. Roth, T. Debaerdemaeker, H.M. Schiebel, J. Organomet. Chem. 402 (1991) 435.

[46] H.A. Brune, H. Roth, G. Schmidtberg, J. Organomet. Chem. 412 (1991) 237.

[47] T. Debaerdemaeker, H. Roth, H.A. Brune, J. Organomet. Chem. 412 (1991) 243.

[48] R.H. Grubbs, A. Miyashita, J. Am. Chem. Soc. 100 (1978) 7418.

[49] M. Green, J.A.K. Howard, P. Mitprachachon, M. Pfeffer, J.L. Spencer, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1979) 306.

[50] K.W. Chiu, J. Fawcett, W. Henderson, R.D.W. Kemitt, D.R. Russell, J. Chem. Soc. Chem. Commun. (1986) 41.

[51] K.W. Chiu, J. Fawcett, W. Henderson, R.D.W. Kemitt, D.R. Russell, J. Chem. Soc. Dalton Trans. (1987) 733.

[52] W. Henderson, R.D.W. Kemmitt, J. Fawcett, L.J.S. Prouse, R.D. Russell, J. Chem. Soc. Chem. Commun. (1986) 1791.

[53] (a) H.J.R. de Boer, G. Schat, O.S. Akkerman, F. Bickelhaupt, J. Organomet. Chem. 321 (1987) 291. (b) H.J.R. de Boer, G. Schat, O.S. Akkerman, F. Bickelhaupt, M. deWit, C.H. Stam, Organometallics 8 (1989) 1288.

[54] B. Patzke, A. Stanger, Organometallics 15 (1996) 2633.

[55] G.W. Parshall, Acc. Chem. Res. 3 (1970) 139.

[56] J. Dehand, M. Pfeffer, Coord. Chem. Rev. 18 (1976) 327.

[57] G.R. Newkome, W.E. Puckett, U. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.

[58] A.D. Ryabov, Chem. Rev. 90 (1990) 403.

[59] P. Foley, G.M. Whitesides, J. Am. Chem. Soc. 101 (1979) 2732.

[60] P. Foley, R. DiCosimo, G.M. Whitesides, J. Am. Chem. Soc. 102 (1980) 6713.

[61] S.S. Moore, R. DiCosimo, A.F. Sowinski, G.M. Whitesides, J. Am. Chem. Soc. 103 (1981) 948.

[62] R. DiCosimo, S.S. Moore, A.F. Sowinski, G.M. Whitesides, J. Am. Chem. Soc. 104 (1982) 124.

[63] S.D. Chappell, D.J. Cole-Hamilton, J. Chem. Soc. Chem. Commun. (1980) 38.

[64] S.D. Chappell, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (1983) 1051.

[65] D.C. Griffiths, G.B. Young, Polyhedron 2 (1983) 1095.

[66] D.C. Griffiths, G.B. Young, Organometallics 8 (1986) 875.

[67] B.C. Ankianec, D.T. Hardy, S.K. Thomson, W.N. Watkins, G.B. Young, Organometallics 11 (1992) 2591.
[68] B.C. Ankianec, V. Christov, D.T. Hardy, S.K. Thomson, G.B. Young, J. Am. Chem. Soc. 116 (1994) 9963.
[69] D.C. Griffiths, D.I. MacTavish, N.A.H. Male, D.A. Tocher, G.B. Young, J. Chem. Soc. Dalton Trans. (1997) 3373.
[70] A. Miyashita, M. Ohyoshi, H. Shitara, H. Nohira, J. Organomet. Chem. 338 (1988) 103.
[71] E. Carmona, M. Paneque, M.L. Poveda, E. Gutiérrez-Puebla, A. Monge, Polyhedron 8 (1989) 1069.
[72] H.F. Klein, A. Bickelhaupt, B. Hammerschmitt, U. Flörke, H.J. Haupt, Organometallics 13 (1994) 2994.
[73] H.F. Klein, A. Bickelhaupt, T. Jung, G. Cordier, Organometallics 13 (1994) 2557.
[74] M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 346 (1988) C27.
[75] M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 437 (1992) 369.
[76] M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 425 (1992) 151.
[77] W.D. Jones, F.J. Feher, Acc. Chem. Res. 22 (1989) 91.
[78] M.R. Chin, S.L. Dong, M.G. Duckett, H.G. Partridge, W.D. Jones, R.N. Perutz, J. Am. Chem. Soc. 115 (1993) 7685.
[79] C.H. Liu, C.S. Li, C.H. Cheng, Organometallics 13 (1994) 18.
[80] J.A. López, Ph.D. Thesis, Universidad de Sevilla, Sevilla, Spain, 1997.
[81] J. Cámpora, J.A. López, P. Palma, P. Valerga, E. Spillner, E. Carmona, Ang. Chem. Int. Ed. Engl. 38 (1999) 147.
[82] J. Vicente, J.A. Abad, R. Bergs, P.G. Jones, D. Bautista, J. Chem. Soc. Dalton Trans. (1995) 3093.
[83] C.F.H. Tipper, J. Chem. Soc. (1955) 2045.
[84] A.D. Walsh, Trans. Faraday Soc. 45 (1949) 179.
[85] D.M. Adams, J. Chatt, R.G. Guy, Proc. Chem. Soc. (1960) 179.
[86] D.M. Adams, J. Chatt, R.G. Guy, J. Chem. Soc. (1961) 738.
[87] N.A. Bailey, R.D. Gillard, M. Keeton, R. Mason, D.R. Russell, J. Chem. Soc. Chem. Commun. (1966) 396.
[88] R.D. Gillard, M. Keeton, R. Mason, M.F. Pillbrough, D.R. Russell, J. Organomet. Chem. 33 (1971) 247.
[89] M. Graciani, M. Lenarda, R. Ros, U. Bellucco, Coord. Chem. Rev. 16 (1975) 35.
[90] R.J. Puddephatt, M.A. Quyser, C.F.H. Tipper, J. Chem. Soc. Chem. Commun. (1976) 626.
[91] F.J. McQuillin, K.G. Powell, J. Chem. Soc. Dalton Trans. (1972) 2123.
[92] M. Lenarda, R. Ros, M. Graciani, U. Bellucco, J. Organomet. Chem. 65 (1972) 407.
[93] G. Pellizer, M. Graciani, M. Lenarda, R. Ganzerla, Inorg. Chim. Acta 145 (1988) 219.
[94] J. Rajaram, J.A. Ibers, J. Am. Chem. Soc. 100 (1978) 829.
[95] M. Lenarda, R. Ros, M. Graciani, U. Bellucco, J. Organomet. Chem. 46 (1972) C29.
[96] D.J. Yarrow, J.A. Ibers, M. Lenarda, M. Graciani, J. Organomet. Chem. 70 (1974) 133.
[97] E.S. Kline, R.H. Hauge, Z.H. Kafafi, J.L. Margrave, Organometallics 7 (1988) 1512.
[98] S.. Wong, S.J. Singer, W.D. Pitts, S.F. Watkins, W.H. Baddley, J. Chem. Soc. Chem. Commun. (1972) 672.
[99] M. Lenarda, N. Bresciani-Pahor, M. Calligaris, L. Randaccio, M. Graziani, Inorg. Chim. Acta 26 (1978) 29.
[100] S. Forcolin, G. Pellicer, M. Graziani, M. Lenarda, R. Ganzerla, J. Organomet. Chem. 194 (1980) 203.
[101] R. Neidlein, A. Rufinska, H. Schwager, G. Wilieg, Agnew. Chem. Int. Ed. Engl. 25 (1986) 640.
[102] R. Mynott, R. Neidlein, H. Schwager, G. Wilke, Agnew. Chem. Int. Ed. Engl. 25 (1986) 367.
[103] D. Bläser, R. Boese, W.A. Brett, P. Rademacher, H. Schwager, A. Stanger, K.P.C. Vollhardt, Agnew. Chem. Int. Ed. Engl. 28 (1989) 206.
[104] C. Kruger, G. Laakman, G. Schroth, H. Schwager, G. Wilke, Chem. Ber. 120 (1987) 471.
[105] H. Schwager, C. Krüger, R. Neidlein, G. Wilke, Agnew. Chem. Int. Ed. Engl. 26 (1987) 1.
[106] H. Schwager, R. Benn, G. Wilke, Agnew. Chem. Int. Ed. Engl. 26 (1987) 67.
[107] P.J. Stang, L. Song, B. Halton, J. Organomet. Chem. 388 (1990) 215.

[108] G.K. Barker, M. Green, J.A.K. Howard, J.L. Spencer, F.G.A. Stone, J. Am. Chem. Soc. 98 (1976) 3373.
[109] G.K. Barker, M. Green, J.A.K. Howard, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1978) 1839.
[110] E.R. Hamner, R.D.W. Kemmitt, M.A.R. Smith@ J. Chem. Soc. Chem. Commun. (1974) 841.
[111] R.J. Gardner, A. Cartner, R.G. Cunninghame, B.H. Robinson, J. Chem. Soc. Dalton Trans. (1975) 2582.
[112] H. Hoberg, A. Herrera, Agnew. Chem. Int. Ed. Engl. 19 (1980) 927.
[113] H. Hoberg, A. Herrera, Agnew. Chem. Int. Ed. Engl. 20 (1981) 876.
[114] H. Hoberg, A. Herrera, Synthesis, (1981) 831.
[115] J.J. Eisch, A.H. Piotrowski, K.I. Han, C. Krüger, Y.H. Tsay, Organometallics 4 (1985) 224.
[116] N.A. Grabowski, R.P. Hughes, B.S. Haynes, A.L. Rheingold, J. Chem. Soc. Chem. Commun. (1986) 1694.
[117] R.H. Grubbs, A. Miyashita, J. Organomet. Chem. 161 (1978) 371.
[118] P.S. Braterman, J. Chem. Soc. Chem. Commun. (1979) 70.
[119] R.H. Grubbs, A. Miyashita, J. Chem. Soc. Chem. Commun. (1977) 864.
[120] P.W. Jolly, G. Wilke, The Organic Chemistry of Nickel, vol. 2, Academic Press, London, 1975.
[121] W. Keim, A. Behr, M. Röper, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon Press, Oxford, 1982, p. 371.
[122] J.C.M. Sinema, G.H.B. Fendesak, H. tomDieck, J. Organomet. Chem. 390 (1990) 237.
[123] W. Bonrath, S. Michaelis, K.R. Pörschke, B. Gabor, R. Mynott, C. Kruger, J. Organomet. Chem. 397 (1990) 255.
[124] S. Michaelis, K.R. Pörschke, R. Mynott, R. Goddard, C. Kruger, J. Organomet. Chem. 426 (1992) 131.
[125] K.R. Pörscke, Agnew. Chem. Int. Ed. Engl. 26 (1987) 1288.
[126] N. Carr, D.F. Mullica, E.L. Sappenfield, F.G.A. Stone, Organometallics 13 (1994) 1666.
[127] C. Stephan, C. Munz, H. tomDieck, J. Organomet. Chem. 468 (1994) 273.
[128] P.W. Jolly, C. Krüger, R. Salz, J.C. Seukutowski, J. Organomet. Chem. 165 (1979) C39.
[129] P. Binger, M.J. Doyle, R. Benn, Chem. Ber. 116 (1983) 1.
[130] D.J. Pasto, N.Z. Huang, Organometallics 4 (1985) 1386.
[131] L. Stehling, G. Wilke, Agnew. Chem. Int. Ed. Engl. 24 (1985) 496.
[132] C.S. Cundy, M. Green, F.G.A. Stone, J. Chem. Soc. (A) (1970) 1647.
[133] J. Browning, C.S. Cundy, M. Green, F.G.A. Stone, J. Chem. Soc. (A) (1971) 448.
[134] J. Browning, M. Green, B.R. Penfold, J.L. Spencer, F.G.A. Stone, J. Chem. Soc. Chem. Commun. (1973) 31.
[135] J. Browning, M. Green, J.L. Spencer, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1974) 97.
[136] H.C. Clark, A. Shaver, Can. J. Chem. 53 (1975) 3462.
[137] J.L. Davidson, R. Herak, L. Manojlovic-Muir, K.W. Muir, D.W.A. Sharp, J. Chem. Soc. Chem. Commun. (1973) 865.
[138] K. Itoh, in: M. Tsutsui, Y. Ishii, H. Yaozeng (Eds.), Fundamental Research in Organometallic Chemistry, Science Press and Van Nostrand Reinhold Company, New York, 1982, p. 149.
[139] A. Moseley, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1971) 1604.
[140] K. Moseley, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1974) 169.
[141] T.S. Ito, S. Hasegawa, Y. Takashi, Y. Ishii, J. Chem. Soc. Chem. Commun. (1972) 629.
[142] H. tomDieck, C. Munz, C. Müller, J. Organomet. Chem. 384 (1990) 243.
[143] (a) H. Suzuki, K. Itoh, Y. Ishii, K. Simon, J.A. Ibers, J. Am. Chem. Soc. 98 (1976) 8494. (b) C. Stephan, H. tomDieck, J. Mol. Catal. 81 (1993) 313.
[144] (a) H. tomDieck, C. Munz, C.J. Müller, J. Organomet. Chem. 384, (1990) 243. (b) R. Dierks, L. Stamp, H. tomDieck, Chem. Ber. 117 (1984) 1913.
[145] M.J. Doyle, J. McMeeking, P. Binger, J. Chem. Soc. Chem. Commun. (1976) 376.
[146] P. Binger, M.J. Doyle, J. McMeeking, C. Krüger, Y.H. Tsay, J. Organomet. Chem. 135 (1977) 405.
[147] P. Binger, M.J. Doyle, J. Organomet. Chem. 162 (1978) 195.
[148] P. Binger, H.M. Büch, R. Benn, R. Mynott, Agnew. Chem. Int. Ed. Engl. 21 (1982) 62.
[149] A.S.K. Hasumi, F. Naumann, M. Bolte, Organometallics 17 (1998) 2385.

[150] W.R. Winchester, M. Gawron, G.J. Palenik, W.M. Jones, Organometallics 4 (1985) 1894.
[151] H.M. Büch, P. Binger, R. Benn, A. Rufinsk, Organometallics 6 (1987) 1130.
[152] W. Kaschube, W. Schröder, K.R. Pörschke, K. Angermund, C. Krüge, J. Organomet. Chem. 389 (1990) 399.
[153] M.A. Bennett, M.P. Schwemlei, Agnew. Chem. Int. Ed. Engl. 28 (1989) 1296.
[154] W.H. Jones, J. Klosin, Adv. Organomet. Chem. 42 (1998) 147.
[155] M.A. Bennett, T.W. Hambley, N.K. Roberts, G.B. Robertson, Organometallics 4 (1985) 1992.
[156] M.A. Bennett, D. Griffiths, T. Okano, V. Parthasarathi, G. Robertson, J. Am. Chem. Soc. 112 (1990) 7047.
[157] M.A. Bennett, E. Wenger, Organometallics 14 (1995) 1267.
[158] M.A. Bennett, D.C.R. Hockless, E. Wenger, Organometallics 14 (1995) 2091.
[159] M.A. Bennett, M. Glewis, D.C.R. Hockless, E. Wenger, J. Chem. Soc. Dalton Trans. (1997) 3105.
[160] M.A. Bennett, E. Wenger, Organometallics 15 (1996) 5536.
[161] J. Klosin, K.A. Abboud, W.M. Jones, Organometallics 14 (1985) 2892.
[162] C. Munz, C. Stephan, H. tomDieck, J. Organomet. Chem. 395 (1990) C42.
[163] C. Munz, C. Stephan, H. tomDieck, J. Organomet. Chem. 407 (1991) 413.
[164] M.A. Bennett, D.C.R. Hockless, M.G. Humphrey, M. Shulz, E. Wenger, Organometallics 15 (1996) 928.
[165] M.A. Bennett, T. Yoshida, J. Am. Chem. Soc. 100 (1978) 1750.
[166] C. Carfagna, R. Galarini, A. Musco, R. Santi, Organometallics 10 (1991) 3956.
[167] C. Carfagna, R. Galarini, K. Linn, J.A. López, C. Mealli, A. Musco, Organometallics 12 (1993) 3019.
[168] H.M.R. Hoffmann, A.R. Otte, A. Wilde, S. Menzer, D.J. Williams, Agnew. Chem. Int. Ed. Engl. 34 (1995) 100.
[169] A. Aranyos, K.J. Szabó, A.M. Castaño, J.E. Bäckvall, Organometallics 16 (1997) 1058.
[170] V. Plantevin, P.W. Blosser, J.C. Gallucci, A. Wojcicki, Organometallics 13 (1994) 3651.
[171] T.M. Huang, R.H. Hsu, C.S. Yang, J.T. Chen, G.H. Lee, Y. Wang, Organometallics 13 (1994) 3657.
[172] P.W. Blosser, D.G. Schimpff, J.C. Gallucci, A. Wojcicki, Organometallics 12 (1993) 1993.
[173] M.W. Baize, V. Plantevin, J.C. Gallucci, A. Wojcicki, Inorg. Chim. Acta 235 (1995) 1.
[174] Y.C. Cheng, Y.K. Chen, T.M. Huang, C.I. Yu, G.H. Lee, Y. Wang, J.T. Chen, Organometallics 17 (1998) 2953.
[175] J.D. Brandshaw, L. Guo, C.A. Tessier, W.J. Youngs, Organometallics 15 (1996) 2582.
[176] R.D.W. Kemmitt, S. Mason, M.R. Moore, J. Fawcett, D.R. Russell, J. Chem. Soc. Chem. Commun. (1990) 1535.
[177] K.W. Chiu, J. Fawcett, W. Henderson, R.D.W. Kemmitt, D.R. Russell, J. Chem. Soc. Dalton Trans. (1987) 733.
[178] R. McCrindle, G. Ferguson, A.J. McAlees, J. Chem. Soc. Chem. Commun. (1990) 1524.
[179] J.F. Hoover, J.M. Stryker, J. Am. Chem. Soc. 111 (1989) 6466.
[180] S. Takahashi, Y. Suzuki, K. Sonogashira, N. Haghiara, J. Chem. Soc. Chem. Commun. (1976) 840.
[181] P.T. Matsunaga, J.C. Mauropoulos, G.L. Hillhouse, Polyhedron 14 (1995) 175.
[182] P.T. Matsunaga, G.L. Hillhouse, J. Am. Chem. Soc. 115 (1993) 2075.
[183] N.A. Bailey, S.E. Hull, R.W. Jotham, S.F.A. Kettle, J. Chem. Soc. Chem. Commun. (1971) 282.
[184] J.K. Stille, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of the Metal–Carbon Bonds, vol. 2, Wiley, New York, 1985, p. 625.
[185] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[186] G.K. Anderson, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), R.J. Puddephatt (Vol. Ed.), Comprehensive Organometallic Chemistry II, Vol 9, Pergamon, Oxford, 1995, p. 431.
[187] A.K. Cheetham, R.J. Puddephatt, A. Zalkin, D.H. Templeton, L.K. Templeton, Inorg. Chem. 15 (1976) 2997.
[188] S. Tangestaninejead, M. Rashidi, R.J. Puddephatt, J. Organomet. Chem. 412 (1991) 445.
[189] M. Rashidi, A.R. Esmaeilbeig, N. Shahabadi, S. Tangestaninejad, R.J. Puddephatt, J. Organomet. Chem. 568 (1998) 53.

[190] R.J. Klinger, J.C. Huffman, J.K. Kochi, J. Am. Chem. Soc. 104 (1982) 2147.
[191] J.F. Hoover, J.M. Stryker, Organometallics 8 (1989) 2973.
[192] M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 346 (1988) C27.
[193] M. Catellani, B.E. Mann, J. Organomet. Chem. 390 (1990) 251.
[194] G. Bocelli, M. Catellani, S. Ghelli, J. Organomet. Chem. 458 (1993) C12.
[195] A.J. Canty, P.R. Traill, J. Organomet. Chem. 435 (1992) C8.
[196] A.J. Canty, J.L. Hoare, N.W. Davis, P.R. Traill, Organometallics 17 (1998) 2046.
[197] A.J. Canty, H. Jin, A.S. Roberts, B.W. Skelton, P.R. Traill, A.H. White, Organometallics 14 (1995) 199.
[198] A.J. Canty, S.D. Fritsche, H. Jin, B.W. Skelton, A.H. White, J. Organomet. Chem. 490 (1995) C18.
[199] A.J. Canty, H. Jin, A.S. Roberts, B.W. Skelton, A.H. White, Organometallics 15 (1996) 5713.
[200] A. Milet, A. Dedieu, A.J. Canty, Organometallics 16 (1997) 5331.
[201] A.J. Canty, H. Jin, B.W. Skelton, A.H. White, J. Organomet. Chem. 503 (1995) C16.
[202] M. Catellani, M.C. Fagnola, Agnew. Chem. Int. Ed. Engl. 33 (1994) 2421.
[203] R.A. Burch, J.C. Calabrese, S.D. Ittel, Organometallics 7 (1988) 1642.
[204] T.J. McCarthy, R.G. Nuzzo, G.M. Whitesides, J. Am. Chem. Soc. 103 (1981) 3396.
[205] F. Ozawa, T. Ito, A. Yamamoto, J. Am. Chem. Soc. 102 (1980) 6457.
[206] S. Komiya, Y. Marimoto, A. Yamamoto, T. Yamamoto, Organometallics 1 (1982) 1528.
[207] G.B. Young, G.M. Whitesides, J. Am. Chem. Soc. 100 (1978) 5808.
[208] T.M. Miller, G.M. Whitesides, Organometallics 5 (1986) 1473.
[209] R. DiCosimo, G.M. Whitesides, J. Am. Chem. Soc. 104 (1982) 3601.
[210] R.J. McKinney, D.L. Thorn, R. Hoffmann, A. Stockis, J. Am. Chem. Soc. 103 (1981) 2595.
[211] A. Peluso, D.R. Salahub, A. Goursot, Inorg. Chem. 29 (1990) 1544.
[212] F. Kawataka, Y. Kayaki, I. Shimizu, A. Yamamoto, Organometallics 13 (1994) 3517.
[213] A. Yamamoto, J. Organomet. Chem. 500 (1995) 337.
[214] R.J. Al-Essa, R.J. Puddephatt, M.A. Quyser, C.F.H. Tipper, J. Am. Chem. Soc. 101 (1979) 364.
[215] S.M. Ling, R.J. Pudepphatt, J. Chem. Soc. Chem. Commun. (1982) 412.
[216] K.B. Wiberg, J.V. McClusky, G.K. Schulte, Tetrahedron Lett. 27 (1986) 3083.
[217] K. Ikura, I. Rhu, N. Kambe, N. Sonoda, J. Am. Chem. Soc. 114 (1992) 1520.
[218] Z. Ye, M. Dimke, P.W. Jennings, Organometallics 12 (1993) 1026.
[219] J.T. Burton, R.J. Pudephatt, Organometallics 5 (1986) 1312.
[220] P.W. Jennings, R.E. Ekeland, M.D. Waddington, T.W. Hanks, J. Organomet. Chem. 285 (1985) 429.
[221] K.J. Cavell, Coord. Chem. Rev. 155 (1996) 209.
[222] P.W.N.M. van Leeuwen, C.S. Roobek, H. van der Heijden, J. Am. Chem. Soc. 116 (1994) 12117.
[223] P.W.N.M. van Leeuwen, C.S. Roobek, Rec. Trav. Chim. Pays-Bas 114 (1995) 73.
[224] J. Cámpora, E. Gutiérrez, A. Monge, P. Palma, M.L. Poveda, C. Ruiz, E. Carmona, Organometallics 13 (1994) 1728.
[225] A. Miyashita, H. Shitara, H. Nohira, J. Chem. Soc. Chem. Commun. (1985) 850.
[226] P.E. Garrou, R.F. Heck, J. Am. Chem. Soc. 98 (1976) 4115.
[227] H. Hoberg, A. Herrera, Chem. Ber. 114 (1981) 831.
[228] H.J. Winter, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of the Metal–Carbon Bonds, vol. 3, Wiley, New York, 1985, p. 259.
[229] J.P. Collman, L.S. Hegedus, L.S. Norton, R.G. Finke, Principles, Applications of Organometallic Chemistry, University Science Books, Mill Valey CA, 1987, p. 870.
[230] J. Cámpora, A. Llebaría, J.M. Moretó, M.L. Poveda, E. Carmona, Organometallics 12 (1993) 4032.
[231] J.M. Huggins, R.G. Bergman, J. Am. Chem. Soc. 103 (1981) 3002.
[232] H.F. Klein, L. Reitze, Chem. Ber. 121 (1988) 1115.
[233] E.G. Samsel, J.R. Norton, J. Am. Chem. Soc. 106 (1984) 5505.
[234] D.B. Grostahn, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 756.

[235] J. Cámpora, E. Carmona, E. Gutiérrez-Puebla, M.L. Poveda, C. Ruiz, Organometallics 7 (1988) 2577.
[236] J. Cámpora, E. Carmona, P. Palma, M.L. Poveda@ J. Chem. Soc. Perkin Trans. I (1990) 180.
[237] M.G. Mason, P.N. Swepston, J.A. Ibers, Inorg. Chem. 22 (1983) 415.
[238] P. Diversi, G. Ingrosso, A. Lucherini, T. Lumini, F. Marchetti, S. Merlino, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1988) 461.
[239] A. Wojcicki, Adv. Organomet. Chem. 12 (1974) 32.
[240] A. Wojcicki, Adv. Organomet. Chem. 11 (1973) 18.
[241] M. Rashidi, N. Sahahbadi, A.R. Esmaelbeig, M. Joshaghani, R.J. Puddephatt, J. Organomet. Chem. 484 (1994) 53.
[242] K. Koo, G.L. Hillhouse, Organometallics 17 (1998) 2924.
[243] K. Koo, G.L. Hillhouse, A.L. Rheingold, Organometallics 14 (1995) 456.
[244] W.D. Neilsen, R.D. Larsen, P.W. Jennings, J. Am. Chem. Soc. 110 (1988) 3307.
[245] F.F. Stewart, W.D. Neilsen, R.E. Ekeland, R.D. Larsen, P.W. Jennings, Organometallics 12 (1993) 4585.
[246] P.W. Jennings, R.E. Ekeland, M.D. Waddington, T.W. Hanks, J. Organomet. Chem. 285 (1985) 429.
[247] D.M. Adams, J. Chatt, R.G. Guy, N. Sheppard, J. Chem. Soc. (1961) 738.
[248] S.E. Binns, R.H. Cragg, R.D. Gillard, B.T. Heaton, M.F. Pillbrow, D.R. Russell, J. Chem. Soc. (A) (1969) 1227.
[249] R.D. Gillard, M. Keeton, R. Mason, M.F. Pilbrow, R.D. Russell, J. Organomet. Chem. 33 (1971) 247.
[250] R.J. Al-Essa, R.J. Puddephatt, J. Chem. Soc. Chem. Commun. (1980) 45.
[251] M. Keeton, R. Mason, D.R. Russell, J. Organomet. Chem. 33 (1971) 259.
[252] E. Carmona, E. Gutiérrez-Puebla, A. Monge, M. Paneque, M.L. Poveda, J. Chem. Soc. Chem. Commun. (1991) 149.
[253] T.R. Belderraín, E. Gutiérrez, A. Monge, M.C. Nicasio, M. Paneque, M.L. Poveda, E. Carmona, Organometallics 12 (1993) 4431.
[254] T.R. Belderraín, M.C. Nicasio, M. Paneque, M.L. Poveda, E. Carmona, Gazz. Chim. Ital. 124 (1994) 341.
[255] R.H. Grubbs, A. Miyashita, J. Am. Chem. Soc. 100 (1978) 7416.
[256] P. Binger, A. Brinkmann, P. Wademann, Chem. Ber. 116 (1983) 2920.
[257] T. Takahashi, S. Ito, S. Sakai, Y. Ishii, J. Chem. Soc. Chem. Commun. (1970) 1005.
[258] K. Moseley, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1971) 982.
[259] L.D. Brown, K. Itoh, H. Susuki, K. Hirai, J.A. Ibers, J. Am. Chem. Soc. 100 (1978) 8232.
[260] H. tomDieck, C. Munz, C. Müller, J. Organomet. Chem. 326 (1987) C1.
[261] C. Stephan, C. Munz, H. tomDieck, J. Organomet. Chem. 452 (1993) 223.
[262] K. Tamao, K. Kobayashi, Y. Ito, J. Am. Chem. Soc. 110 (1988) 1288.
[263] K. Tamao, K. Kobayashi, Y. Ito, Synlett (1992) 539.
[264] M. Zhang, S.L. Buchwald, J. Org. Chem. 61 (1996) 4498.
[265] M. Catellani, G.P. Chiusoli, S. Ricotti, J. Organomet. Chem. 296 (1985) C11.
[266] M. Catellani, G.P. Chiusoli, S. Ricotti, F. Sabini, Gazz. Chim. Ital. 115 (1985) 685.
[267] M.A. Huffman, L.S. Liebeskind, J. Am. Chem. Soc. 113 (1991) 2771.
[268] B.M. Trost, M. Lautens, J. Am. Chem. Soc. 107 (1985) 1781.
[269] B.M. Trost, M. Lautens, Tetrahedron Lett. 26 (1985) 4887.
[270] B.M. Trost, G.J. Tanoury, J. Am. Chem. Soc. 109 (1987) 4753.
[271] B.M. Trost, M.K. Trost, Tetrahedron Lett. 32 (1991) 3647.
[272] B.M. Trost, G.J. Tanoury, J. Am. Chem. Soc. 110 (1988) 1636.
[273] B.M. Trost, A.S.K. Hasumi, Agnew. Chem. Int. Ed. Engl. 32 (1993) 1085.
[274] B.M. Trost, M.K. Trost, J. Am. Chem. Soc. 113 (1991) 1850.
[275] M. Catellani, L. Ferioli, Synthesis (1996) 769.
[276] O. Reiser, M. Weber, A. de Meijere, Agnew. Chem. Int. Ed. Engl. 28 (1989) 1037.
[277] K. Albrecht, O. Reiser, M. Weber, A. de Meijere, Tetrahedron 50 (1994) 383.
[278] G. Dyker, Agnew. Chem. Int. Ed. Engl. 33 (1994) 103.

[279] F. Ozawa, T. Hidaka, T. Yamamoto, A. Yamamoto, J. Organomet. Chem. 330 (1987) 253.
[280] F. Ozawa, M. Fujimori, T. Yamamoto, A. Yamamoto, Organometallics 5 (1986) 2144.
[281] M. Catellani, F. Frignani, A. Rangoni, Agnew. Chem. Int. Ed. Engl. 36 (1997) 119.