NICKEL, PALLADIUM, AND PLATINUM

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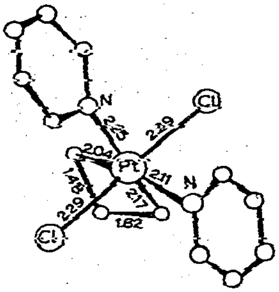
CONTENTS

ABBREVIATIONS

Acac = acetylacetonate
Bipy = 2,2'-bipyridyl
COD = 1,5-cyclooctadiene
Diars = bis-1,2-(methylphenylarsino)ethane
CP = cyclopentadiene
Dias = *o*-phenylenebis(dimethylarsine)
Diphos = bis-1,2-(diphenylphosphino)ethane
Dpb = bis-1,2-(diphenylphosphino)butane
Dpp = bis-1,2-(diphenylphosphino)propane
En = ethylenediamine
Hfacac = hexafluoroacetylacetone
NBD = norbornadiene
Np = neopentyl
Phen = 1,10-phenanthroline
Py = pyridine

I. METAL–CARBON σ-BONDED COMPLEXES

Structural studies have been carried out on several organoplatinum compounds. The previously reported complex, $(PEt_3)_2(OH)PtGePh_3$, has been reformulated as *cis*-$(PEt_3)_2(\sigma\text{-}Ph)Pt\{GePh_2(OH)\}$ as a result of an X-ray crystallographic study[1]. The complex $[C_3H_6PtCl_2]_x$ which results from the interaction of cyclopropane and H_2PtCl_6 reacts with pyridine to give the derivative $\{(C_3H_6)PtPy_2Cl_2\}$ which, in the crystalline state, is suitable for X-ray-analysis structure (1)[2a]. Among the reactions of this complex are the conversion of this compound to [Et(Py)CH] $PyPtCl_2$ by heating in benzene and to [Et(Py)CH] $PyPtCl_4{\cdot}CHCl_3$ by refluxing in chlorocarbon solvents. (**2a**, **2b** are the two forms of the former complex found in the unit cell and **3** is the structure of the latter complex). The mean metal–ligand distances for these complexes have been found to be independent of the formal oxidation state[2b]. The tetrameric complex, $(Et_3PtCl)_4$ (4) is structurally similar to its methyl-platinum analog[3]. The CH_3's of the ethyl groups are held rigid by the steric repulsions within the molecule[3]. $(\pi\text{-}C_5H_5)PtMe_3$ has been found to have a "piano stool" stereochemistry with mean bond lengths: Pt–C(Me), 2.11 Å; Pt–C(π-C_5H_5), 2.32 Å; and C–C, 1.43 Å[4].



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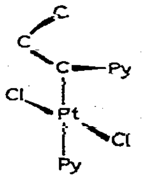

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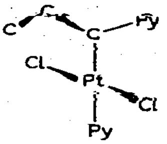

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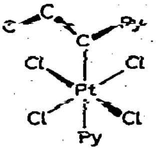

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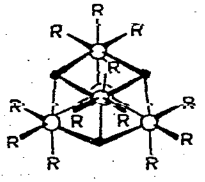


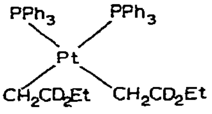
R = Et
○ = Pt
● = Cl

(4)

Morrow and Beauchamp have assigned the stretching vibrations of the Me group in *cis*-$(PPh_3)_2PtMe_2$ as ν_a 2934 cm^{-1}, ν_s 2878 cm^{-1}, and overtone from CH_3 deformation 2806

cm^{-1}, by application of the Average Rule for the isotopically substituted species, Me = CH_3, CH_2D, CHD_2, and CD_3 [5]. Three intense absorptions in the electronic spectra of *trans*-$[L_2M(C{\equiv}CR)_2]$ have been observed where M = Ni or Pt in the range 220–360 nm. (The M = Pd system has unresolved bands at low wavelength). The bathochromic shifts of the lowest energy band increase in the series: $R = H < CH_3 < CH_2F < CH_2{=}CH < HC{\equiv}C < Ph < CH_3C{\equiv}C$ for *trans*-$[(PEt_3)_2Ni(C{\equiv}CR)_2]$; $R = H < CH_3 < HC{\equiv}C < CH_2{=}CH < CH_3C{\equiv}C < Ph < PhC{\equiv}C$ for *trans*-$[(PEt_3)_2Pt(C{\equiv}CR)_2]$; and $R = H < CH_3 < CH_2{=}CH < Ph$ for *trans*-$[(PMe_3)_2Pt(C{\equiv}CR)_2]$. The linear correlation of the position of the band with the ionization potential of the free alkyne has led Masai *et al.* to assign this band to the transition between the molecular orbitals involved in the metal–alkynyl bond. On the basis of the bathochromic shifts and the infrared spectral data for the complexes $(PEt_3)_2M(C{\equiv}CR)_2$ which show a linear correlation between the square of the M–C stretching frequency and Taft's polar constants for R, the authors propose the existence of an extended π-interaction between the two alkynyl groups through the metal[6,7].

The similarity of the mass spectra of *cis*- and *trans*-PtL_2X_2, (L = NH_3, Py; X = Cl, Br, I) has prompted the suggestion that excitation of the complex to a tetrahedral state may occur on electron impact[8]. In other complexes (L = PPh_3) the spectra for *cis*- and *trans*-isomers differ significantly and are different than those of chelated complexes (L_2 = Bipy, or di-α-pyridylmethane, X = Cl)[8].



(5)

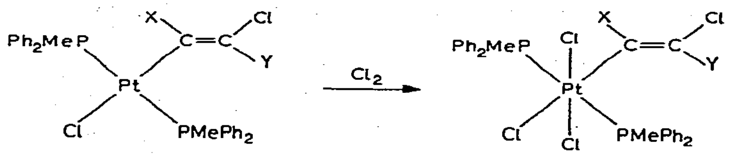
The deuterium decoupled ^1H NMR spectrum of (5) compared to a calculated spectrum and assigned a "*cis*" configuration. The parameters for the spectrum were derived by comparison of theoretically calculated spectra and the observed spectrum of the methylene protons[9]. For *cis*-$[PtMe_2(EMe_2Ph)_2]$ (E = P,As) $J(^{195}Pt{-}^{13}C)$ and $J(^{195}Pt{-}^{1}H)$ values of 594 and 67.1 Hz (E = P), and 685 and 72.2 Hz (E = As) respectively are observed[10]. These results reflect a lower platinum–methyl bond strength in the E = P compound as is also suggested by the lower ν(M–C) stretching frequency for this complex[10].

Polarograms of the species $(H_2O)_3PtMe_3^+$, obtained from $Me_3PtI + AgSO_4$, display four well-separated waves at such negative potentials as to indicate extreme robustness of the complex ion. Supporting evidence for the formulation of a tris-aquated complex ion has been derived from the NMR spectrum[11].

A popular preparative route to metal–σ-carbon complexes is the oxidative addition reaction

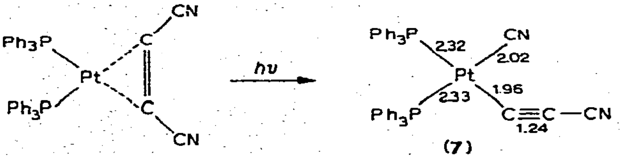
$$M(PR_3)_n + RX \rightarrow RMX(PR_3)_2$$

The order of thermal stability for a series of complexes $(PPh_3)_2Ni(aryl)(X)$ made by this approach was found to be *o*-tolyl > *p*-chlorophenyl > phenyl > *p*-tolyl ≈ *p*-methoxyphenyl > *m*-tolyl[12]. The order of reactivity of organic halides with $Pd(PPh_3)_4$ was found to be PhI > PhBr > PhCl; the PhCl being unreactive at +135°. Electron-withdrawing substituents on R enhance reactivity; *p*-$NO_2C_6H_4Cl$ > *p*-CNC_6H_4Cl > *p*-$PhCOC_6H_4Cl$ > PhCl. It has been suggested that this reaction may be regarded as another example of aromatic nucleophilic substitution in which bond breaking is rate determining[13]. $Pt(PEt_3)_4$ functions as an unusually strong nucleophile for this reaction undergoing oxidative addition with benzonitrile, PhCl, allyl chloride and hydrogen to give *trans*-$(PEt_3)Pt(CN)Ph$, *trans*-$(PEt_3)_2PtCl(Ph)$, (π-allyl)$Pt(PEt_3)_2^+$ and $H_2Pt(PEt_3)_2$ respectively[14]. The oxidative addition of *cis*-1,2-dichloroethylene to $Pt(PMePh_2)_4$ occurs in the presence of ethoxide ions in refluxing ethanol to give the acetylide $(PMePh_2)_2PtCl(C{\equiv}CH)$. It is suggested that strong bases such as the ethoxide ion serve to promote formation of chloroacetylene which then reacts with the Pt^0 complex. *trans*-1,2-Dibromoethylene adds to give the expected product, *trans*-$(PMePh_2)_2Pt(CH{=}CBrH)Br$, which readily eliminates acetylene to give the dibromide. The analogous chlorovinyl complexes will add chlorine to give new platinum(IV) species (6)[15]. *trans*-$(PPh_3)_2PtX$(alkenyl) complexes can also be obtained either by the reaction of $(PPh_3)_4Pt$ and vinylbromide or by the oxidative addition of HX to $(PPh_3)_2$(acetylene)Pt^0, (where X = Cl, O_2CCF_3). Similarly, β-bromostyrene will form *trans*-$[(PMe_2Ph)_2MBr(CH{=}CHPh)$ from the hydrazine reduction of *cis*-$[MCl_2(PMe_2Ph)_2]$ (M = Pd, Pt). ^1H NMR studies have shown that in alkenyl complexes prepared by protonation of acetylene complexes, the metal and proton are *cis* on the multiple bond with protonation according to Markownikoff's rule. With 2-propynylic halides the product is *trans*-$[(PPh_3)_2PtCl(CH{=}C{=}CR^1R^2)]$[16]. Carbon–carbon bond cleavage occurs on oxidative addition of $MeC(CN)_3$ to $Pt(PPh_3)_4$ to give $(PPh_3)_2Pt(CN)[C(CN)_2Me]$[17]. Observation of changes in the infrared spectrum of some dicyanoacetylene compounds after several years storage led to the discovery of their photochemical isomerization to acetylide as verified by X-ray structural analysis on (7)[18].



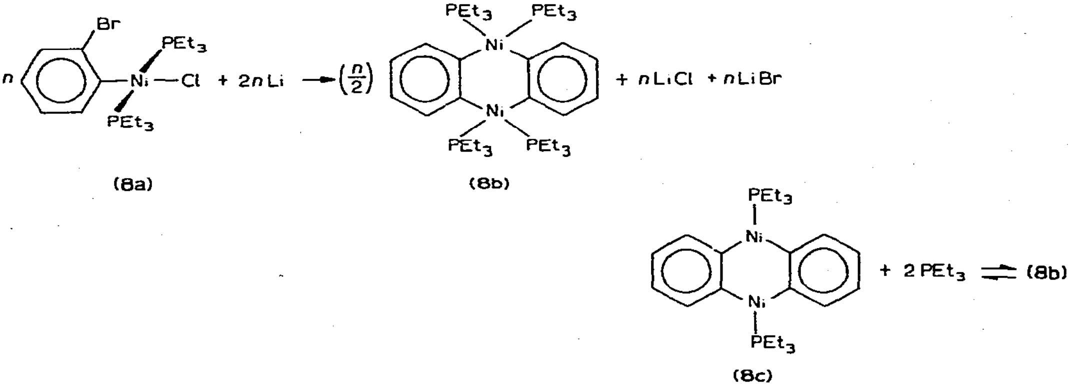
(X,Y = H, Cl)

(6)



(7)

A complex (Dias)PtMe_2, containing a chelating arsine ligand, undergoes oxidative addition with methyl, acyl, or allyl halides to give (Dias)PtMe_2(R)X as readily as the corresponding complexes containing monodentate arsines[19]. Spectral studies have indicated the addition is *trans* for acetyl and benzoyl halides and *cis* for allyl and 2-methylallyl halides. Further, this type of reaction has been shown to be stereospecific by the spectral analysis of the products of the addition to (*rac*-Dias)PtMe_2 and (*meso*-Dias)PtMe_2 [20]. The complex *trans*-$(P\text{-}i\text{-}Pr_3)_2Ni(Me)Cl$ obtained from the corresponding dichloride and MeLi is stable indefinitely at $-6°$ under an inert atmosphere[21] and can undergo metathetical displacement to give the complexes *trans*-$(P\text{-}i\text{-}Pr_3)_2NiMeX$ (X = Br, I). These complexes react with PPh_3 to give $NiX(PPh_3)_3$ (X = Cl, Br, I). The complex $NiMeI(P\text{-}i\text{-}Pr_3)_2$ reacts with methyl iodide to give lustrous red crystals of stoichiometry, $[P\text{-}i\text{-}Pr_3Me]^+[Ni(P\text{-}i\text{-}Pr_3)I_3]^-$. The complex (diphos)$NiCl_2$ and MeLi yield a dimethyl derivative which reacts with phenol to give a stable phenoxy complex (diphos)Ni(Me)OPh[21].



(8a)

(8b)

(8c)

A stoichiometric reaction of lithium metal with (8a) results in abstraction of the *o*-Br to give bright yellow crystals. This product has been assigned the formula, $[C_6H_4Ni(PEt_3)_2]_2$, on the basis of NMR and reactions with I_2 and $Cl_2C{=}CCl_2$. Molecular weight studies in n-butane have been interpreted in terms of the equilibrium (8b) ⇌ (8c) shown[22]. Reactions of the lithium and Grignard reagents of CH_2SiMe_3 (= R) have led Wilkinson and coworkers to a variety of complexes[23]: $Pt_3R_6(SMe_2)_3$ was obtained from *cis*-$PtCl_2(SMe_2)_2$; *cis*-L_2MR_2 from *cis*-L_2MCl_2 (where M = Pt, L = PPh_3, PMe_2Ph, $AsPh_3$ or L_2 = COD; M = Pd, L = PEt_3); and *trans*-$(PEt_3)_2PtHR$ from *trans*-$(PEt_3)_2PtHCl$. In all cases the trimethysilylmethyl ligand gave more stable complexes than the corresponding alkyl and appeared to have a *trans* influence equivalent to cyanide on the basis of the low metal–hydride stretching frequency (ν(Pt–H) 1955 cm^{-1}) and the low coupling constant ($J(^{195}Pt\text{–}^1H)$ 705 Hz at τ 16.8 ppm) in the hydride complex[23]. The complexes *trans*-$L_2Pd(R)X$ (L = $SeEt_2$, $TeEt_2$; R = aryl, and X = halogen) have been prepared from their corresponding dichloride and the appropriate Grignard reagent. The complexes with R = *p*-chloro or *p*-fluorophenyl were unusually stable with stability increasing in the order Cl < Br < I, and $SEt_2 < SeEt_2 < TeEt_2$[24]. For the analogous platinum system stable complexes were formed for L = $TeEt_2$

only. The only disubstituted compound prepared was *trans*-$(TeEt_2)_2Pt(o\text{-tolyl})_2$ [25]. A series of platinum(IV) complexes $(PtX_2Me_2)_n$, X = Cl, Br and I, have been prepared[26]. To generate $(PtBr_2Me_2)_n$, $[IPtMe_3]_4$ was refluxed in liquid bromine with HBr for 8 h. A product analyzing as, $PtMe_3I\cdot PtI_2Me_2$, is obtained from the reaction of K_2PtCl_4 with MeMgI. This complex undergoes reaction with En to give a mixture of $[(PtMe_3En)_2En]I_2$ and $PtI_2Me_2(En)$. The latter complex yields $(PtI_2Me_2)_n$ on treatment with HI or $HClO_4$. The $(PtCl_2Me_2)_n$ may be obtained from the bromide $(PtBr_2Me_2)_n$ by the following reaction sequence

$$(PtBr_2Me_2)_n + Py \rightarrow PtBr_2Me_2(Py)_2$$

$$PtBr_2Me_2(Py)_2 + Cl_2 \xrightarrow{HCCl_3} (PyH)_2(PtCl_4Me_2)$$

$$(PyH)_2PtCl_4Me_2 \xrightarrow[Py]{H_2O} PtCl_4Me_2(Py)_2$$

$$PtCl_2Me_2Py_2 + HClO_4 \rightarrow (PtCl_2Me_2)_n$$

The complexes $(PtX_2Me_2)_n$ are presumably polymeric as evidenced by their insolubility and the presence of both terminal and bridging ν(Pt–X) stretches in the infrared[26].

A σ-carbon bonded palladium β-diketonate complex $[Pd(Acac)_2L]$ has been obtained from addition of L = PPh_3, Py, or $NHEt_2$ to $Pd(Acac)_2$ [27]. $Pd(Acac)_2L$ contains one σ-carbon bonded Acac ligand.

Halpern and Boyd have studied the equilibrium

$$\underset{(A)}{PtCl(PPh_3)_2(CO)^+} + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(B)}{PtCl(PPh_3)_2(COOR)} + H^+$$

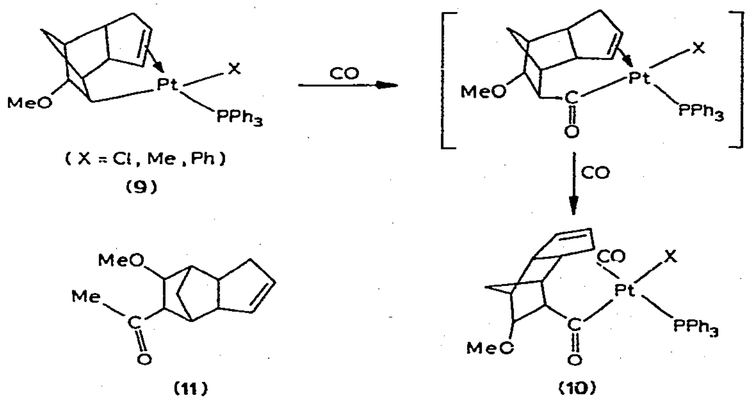
spectrophotometrically at 300 nm using a variety of alcohols[28]. The system follows the rate law:

$$d[PtCl(PPh_3)_2(COOR)]/dt = k_1[A][ROH] - k_{-1}[B][H^+]$$

with k_1 being dependent on ROH over the range (MeOH) $k_1 = 11.1\ M^{-1}\ s^{-1}$ to (2-propanol) $k_1 = 0.68\ M^{-1}\ s^{-1}$. The reverse reaction was relatively insensitive to the nature of R[28]. The cations $[PtX(CO)L_2]^+$ have been prepared from NaX and $[Pt_2Cl_2L_4]^{2+}$ in the presence of CO[29]. $[PtX(CO)L_2]^+$ reacts with H_2O to give *trans*-$PtHXL_2$; and with ROH to give *trans*-$PtX(COOR)L_2$ (X = NO_3, C_6F_5, SCN; L = PPh_3)[29]. Reaction of $M(NCO)_2(Ph_3P)_2$ (M = Pd, Pt) with CO and ROH gives the complexes $(Ph_3P)_2M(NCO)(CO_2R)$. $[(Ph_3P)_2PtX_2Pt(PPh_3)_2]^{2+}$, (X = azide or isocyanate), reacts with CO in CH_2Cl_2 to give the cation $[(Ph_3P)_2PtCO(NCO)]^+$ which in turn can be treated with CO and ROH to give $[(Ph_3P)_2PtCO(COOR)]^+$. The reactions of this latter alkoxycarbonyl cationic complex include displacement of CO by Ph_3P; conversion of

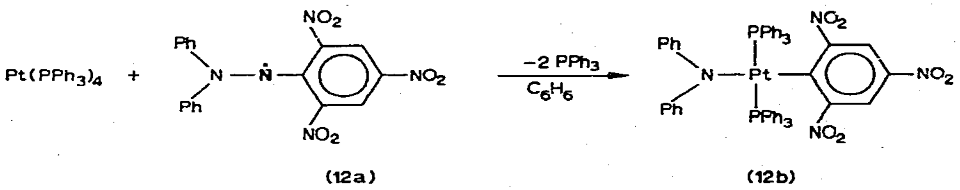
COOR to COOR′ by addition of excess R′OH; and reaction with azide ion to give $(Ph_3P)_2Pt(NCO)(CO_2R)$[30]. The carbonylation of the complexes $(Ph_3P)_2PtN_3X$ ($X = N_3$, NCO, $NHSO_2C_6H_4Me$) in ROH solution also yields $(Ph_3P)_2Pt(NCO)(CO_2R)$[31]. Formation of the alkoxy carbonyl groups is thought to occur via nucleophilic attack by ROH on a coordinated CO group[29,31].

Acyl complexes, *trans*-$PdX(COR)(PPh_3)_2$, (X = Cl, I; R = Me, allyl, vinyl) may be obtained from the oxidative addition of RX to $Pd(CO)(PPh_3)_3$ [32]. In the case of methyl iodide, *cis*- and *trans*-$Pd(Me)(I)(PPh_3)_2$ are formed as side products[32]. The acyl complex **(10)** has been obtained from **(9)** by a slow reaction with CO under mild conditions[33]. The intermediate shown is proposed on the basis of the time dependent infrared spectrum of the reaction mixture. The organic product **(11)** obtained from carbonylation of the palladium analogue of (9) (X = Cl) lends credibility to the proposed structures[33].

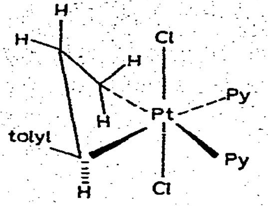


From infrared kinetic studies on the reaction $Pt(CO)Cl(C_2H_5)AsPh_3 + AsPh_3 \rightarrow Pt(COC_2H_5)Cl(AsPh_3)_2$ Mawby and Glyde have proposed a two step mechanism in which the major rate-determining step involves the combination of ethyl and carbonyl to give a propionyl ligand without assistance from solvent or nucleophile[34].

Beck *et al.* have undertaken a study of the oxidative addition reactions of stable organic radicals such as **(12a)** to $(PPh_3)_4Pt^0$ to give products such as **(12b)**[35].



Insertion of platinum into R substituted cyclopropane rings RC_3H_5 was effected by the displacement of C_2H_4 from $(C_2H_4PtCl_2)_2$ with the order of reactivity being R = n-C_6H_{13} > $PhCH_2$ > Ph, (no reaction being observed for R = CO_2Me, COMe, CN)[36]. The insertion is into the 2,3-bond of the ring and occurs in high yield. Only for R = Ph was a minor product due to insertion into the 1,2-bond observed. However for R = *p*-tolyl, the 1,2-derivative is the major product as evidenced by the structure of the bis-pyridine adduct (13). In all cases the structures were assigned on the basis of the NMR of the bis-pyridine derivatives. For *trans*-disubstituted cyclopropanes the stereochemistry of the pyridine derivatives is as in (14) while *cis*-disubstituted cyclopropanes led to isomerization reactions. The differing reaction pathways have been interpreted as indicative that the reaction is not solely determined by differential coordination of the cyclopropane but by the energetics of the subsequent ring opening[36].



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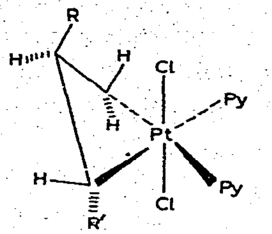
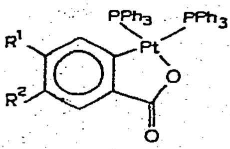


R = R' = Ph
R = *n*-Bu, R' = Me

(14)

Attempts to isolate benzyne–platinum complexes have led to several other platinum compounds[37]. The compound (15) resulted from the reaction of $Pt(PPh_3)_4$ in C_6H_6 with benzenediazonium-2-carboxylates. Extrusion of CO_2 could not be achieved photochemically or thermally even where R_1 and R_2 were labilizing groups. Similar attempts to prepare a benzyne derivative from (16) or (17) also failed but under some conditions did yield triphenylenes presumably formed via organoplatinum intermediates[37]. Reaction of benzenediazonium-2-carboxylate with $(PhC_2)(Cl_3C_2)Ni(PEt_3)_2$ in refluxing CH_2Cl_2 produced (18a) and (18b)[38a]. Neither of these products was obtained in the presence of excess furan. The authors have suggested that benzyne does indeed form in the reaction mixture and that the Ni—C bond adds across the multiple bond in benzyne to give (18a)[38a].

$(PR_3)_2Ni(C{\equiv}CR)H$ complexes have been isolated in low yield from $Ni(Acac)_2$ + Al-i-Bu_3 + $RC{\equiv}CH$ + PR_3 [38b].



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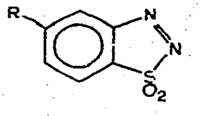

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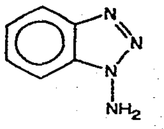

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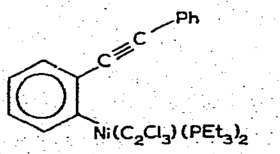

(18a)

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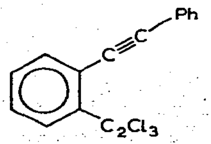
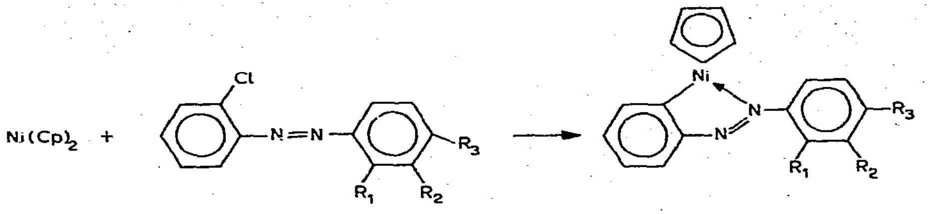


(18b)

Synthesis of hererocyclic nickel compounds has been the topic for a review which includes organonickel complexes[38c].

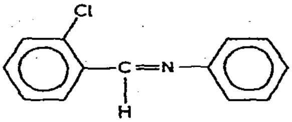
Preparation of systems in which the organometal complex contains a chelating ligand bound via a σ-carbon and a Group VA donor have been reported. Reaction of $Ni(Cp)_2$ with (**19a**) has led to several complexes (**19b**). In (**19b**) with $R_1 = Cl$, $R_2 = R_3 = H$, reaction with a second $Ni(Cp)_2$ molecule can take place to give a binuclear complex. Related products obtained from (**20**), (**21**) and $Ni(Cp)_2$ have also been reported[39,40].

ortho-Palladation of *p*-xylenediamine with $PdCl_4^{2-}$ had led to two binuclear organopalladium derivatives in a ratio of 7/3 which have been assigned the structures (**22**), (**23**) from spectroscopy and chemical reactivity[41].



(19a)

(19b) $R_1 = R_2 = R_3 = H$
$R_1 = H, R_2 = H, R_3 = F$
$R_1 = H, R_2 = F, R_3 = H$



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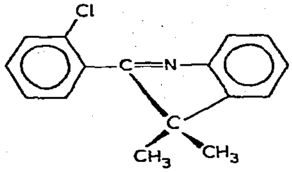

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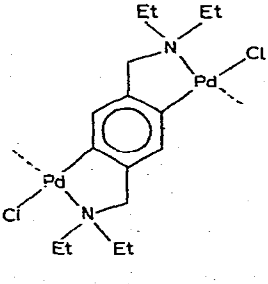
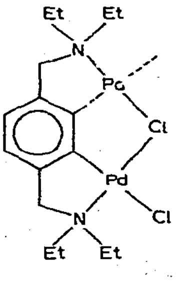
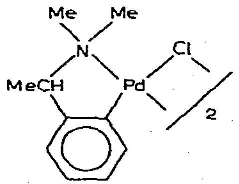


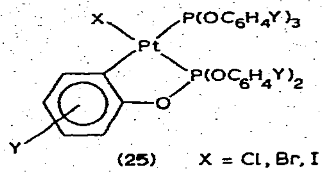




(22) (23) (24)

Some resolution of optically active phosphines has been achieved by the stereospecific coordination of phosphine to an asymmetric palladium complex (24) ($[\alpha]_D^{26}$ +53.4°, (c 1.22, C_6H_6))[42]. A bridge cleavage reaction of (24) with a two fold excess of L = racemic PPh(α-Np)(*o*-tolyl), and PPh(α-Np)(*p*-$EtOC_6H_4$) leaves unreacted phosphine which when isolated from the reaction mixture shows some activity ($[\alpha]_D^{26}$ = +2.39°(c 1.78, CH_2Cl_2) and $[\alpha]_D^{26}$ = −2.57°(c 6.80, CH_2Cl_2) respectively). Displacement of the coordinated phosphine L with diphos yields free L with $[\alpha]_D^{26} = -1.04°$ (*c* 7.72, CH_2Cl_2) and $[\alpha]_D^{26} = +0.91°$ (*c* 6.06, CH_2Cl_2) respectively[42].

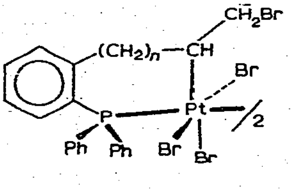
Internal metallation reactions occur on prolonged refluxing of solutions of *trans*-PtX_2L_2 where L is a bulky tertiary phosphine containing t-Bu or *o*-tolyl groups. The tendency to metallate is $X = Cl < Br < I$ and is substantially increased by the presence of lithium salt[43]. The preference for formation of five-membered chelate rings can be seen in the metallation reactions of *trans*-$MX_2[PPh(o\text{-}C_6H_4Me)_2]_2$ which react in the opposite trend for $X(Cl > Br \gg I)$ and the same trend for $M(Pt > Pd)$ as the previous complexes to give the products (25) in which a five-membered chelate ring is formed despite the possibility of attack on the methyl group in the *o*-tolyl phosphite to give a six-membered ring[44]. Similar



(25) $X = Cl, Br, I$
$Y = H, o\text{-}Me, p\text{-}Me, m\text{-}Me$

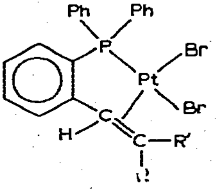
products have also been obtained for Ni, Pd, or Pt by reaction of the 2-(diphenylphosphino)-benzyl potassium salt with L_2MCl_2 ($L = SEt_2, PBu_3$ for $M = Pt$; $L = SEt_2, PEt_3$ for $M = Pd$; and $L = PEt_3$ for $M = Ni$)[45].

The ligands *o*-$CH_2{=}CH(CH_2)_nC_6H_4PPh_2$, $n = 0,1$, form complexes of the type ($PtBr_2$ ligand) which give the insoluble Pt^{IV} complexes (26) on bromination. Alcoholysis of (26) gives methoxy and ethoxy derivatives formulated as $PtBr_2(o\text{-}ROCH{=}CHC_6H_4PPh_2)$, R = Me, Et for $n = 0$, and as (27) for $n = 1$[46].



$n = 0,1$

(26)

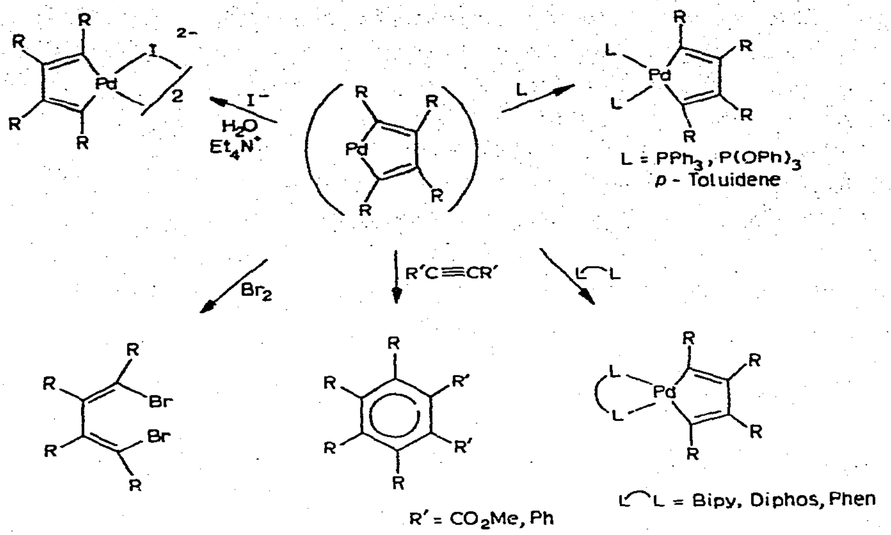


$R = H, R' = CH_2OEt$
$R = Me, R' = OMe$

(27)

In the study of the polymerization of 2-methyl-3-butyn-2-ol to linear polymers (mol. wt ca. 1700) in the presence of *cis*-$(PPh_3)_2PtCl_2$ the complexes [*trans*-$(PPh_3)_2Pt[C{\equiv}CC(CH_3)_2OH]_2$] and (*trans*-$(PPh_3)_2PtCl[C{\equiv}C{-}C(CH_3)_2OH]$) have been isolated and identified as being analogous to the intermediates in the polymerization of phenylacetylene[47]. The complexes were identified by comparison of the UV spectra with the analogous $(PPh_3)_2Pt$ phenylacetylides[48].

Dibenzylideneacetone has been found to form Pd^0 and Pt^0 complexes which are suitable reagents for further reaction with substituted acetylenes[49,50]. In the trimerization of

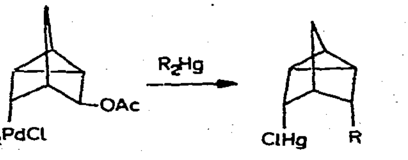


Scheme 1. Reactions of the palladiacyclopentadiene moiety.

RC≡CR (R = CO_2Me) to hexamethylmellitate a novel palladiacyclopentadiene intermediate has been isolated (see Scheme 1).

Benzonitrile reacts with $(Bipy)Ni(Et)_2$ to give a $(Bipy)Ni(PhCN)_2$ (which is an active catalyst polymerizing acrylonitrile) and n-butane[51]. Thermal stability of $(Bipy)NiR_2$ is R = Me > Et > allyl > Bu and the decomposition is first order. Olefins will also displace R to give $BipyNi(olefin)_2$. The unstable intermediate $[R_2Ni(Bipy)olefin]$ has also been isolated for olefin = acrolein or acrylonitrile. Both the intermediate and the product have a π-bonded olefin. The stability constants for the products and intermediates have been determined for various R's and olefins[52,53].

The reaction of (28) with organomercury compounds yields a coupled product and a mercury complex[54].



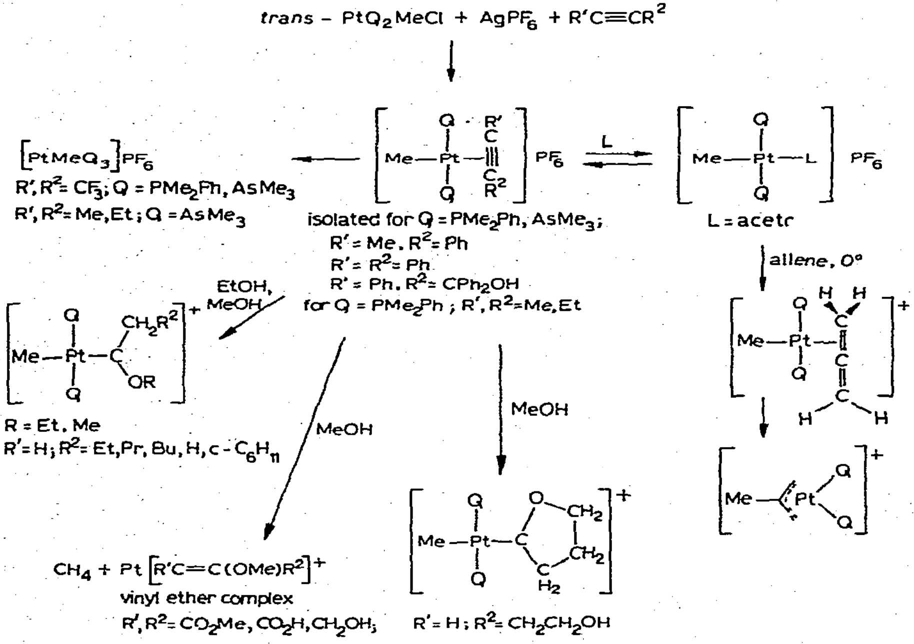
(28) R = Ph, CH=CHMe$_2$

Comparison of the rate of spontaneous conversion of *cis*-$(PEt_3)_2PtCl$(*o*-tolyl) to the *trans* compound in alcohol and the rate of substitution of chloride by CN^- or I^- has been made. The substitution reaction follows a rate law, $k_{obs} = k_1 + k_2[X^-]$ with k_1 being two orders of magnitude larger than k_i the specific rate constant for the approach to isomer equilibrium which is a first order process[55].

The reaction of *trans*-$[Q_2PtMeCl]$ (Q = phosphine or arsine) with RCN and AgX in alcohol has been found to give cationic nitriles, π-nitriles, and imino ether complexes depending on the nature of the reagents and solvent[56,57]. Aryl nitriles favour the formation of normal nitrile complexes. With perfluoroaryl nitriles, imino ether complexes can form depending on the nature of the anion $X = BF_4^- \gg PF_6^- \sim SbF_6^-$ and of the alcohol, $MeOH > EtOH > n\text{-}PrOH \gg (CF_3)_2CHOH \sim Me_2CHOH \sim Me_2CO$. In the case of NCC_6F_4CN with $(PMe_2Ph)_2PtMeCl$ and $AgBF_4$ in EtOH, the product has been described as a π-nitrile, $\{PtMe(PMe_2Ph)_2[\pi\text{-}NCC_6F_4C(OEt){=}NH]PtMe(PMe_2Ph)_2\}(BF_4)_2$. Since refluxing a σ-nitrile complex in MeOH yields no imino ether after 6 hours, Clark et al. have proposed that this product results from the nucleophilic attack of the alcohol on a π-nitrilic intermediate.

II. METAL—CARBENE COMPLEXES

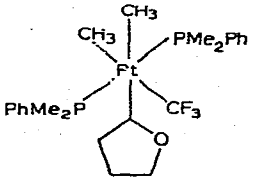
The cationic π-acetylene complexes $[PtMe(R^1C{\equiv}CR^2)Q_2]$ are highly susceptible to nucleophilic attack by alcohols to give alkoxy—carbene complexes of the type shown in Scheme 2[58,59,60]. The cationic species "$[PtCF_3(R^1C{\equiv}CR^2)Q_2]$" results in the polymerization of $R^1C{\equiv}CR^2$. In non-nucleophilic solvents a tetramethylcyclobutadiene complex may be isolated, *e.g.* $[PtCF_3(C_4Me_4)(PMe_2Ph)_2]PF_6$, together with polymer. The platinum(IV) complex, $PtMe_2(CF_3)(PMe_2Ph)_2I + AgPF_6$ gives a species which readily



Scheme 2. Reactions of the species $[MePtQ_2(R^1C{\equiv}CR^2)]^+$.

polymerizes acetylenes. With $CH{\equiv}CCH_2CH_2OH$ in acetone (29) is isolated[61]. Reaction of $[PtHX(Me_2PhP)_2]$ with $AgPF_6$ in the presence of "base" and C_2H_4 yields the products *trans*-$[PtEt(Me_2PhP)_2(base)]^+PF_6^-$ (base = CO; 2,4,6-trimethylpyridine, or carbene)[62].

Nucleophilic attack by LH on coordinated isocyanides in the cations, $[Pt(CNEt)_2(PMe_2Ph)_2](PF_6)_2$ and *trans*-$[PtX(CNR)(PEt_3)_2]ClO_4$ give the carbenes; *trans*-$[Pt(EtNC)(PMe_2Ph)_2\{C(NHEt)L\}](PF_6)_2$ (L = EtO, *p*-MeC_6H_4NH, PhNH, $PhCH_2S$)[63] and *trans*-$[PtX\{C(NHR)L\}]ClO_4$ (L = PhNH, EtNH, EtO; X = Cl, Br; R = Ph, Me)[64]. Alkyl alcohol or primary amines react with the neutral isocyanide complex, *cis*-$PtX_2(RNC)(PR_3)$, (PR_3 = PEt_3, PEt_2Ph, PMe_2Ph; X = Cl, Br, I; R = Ph, Me) to give the *cis*-platinum carbene complexes[65]. The corresponding palladium complexes *cis*-$PPh_3PdCl_2(PhNC)$ have been treated with $HgPh_2$, $PbPh_4$, $PbPh_3Cl$, $SnPh_4$ and $BiPh_3$ to give (30) which will undergo bridge cleavage and protonation to give carbene compounds (31)[66].



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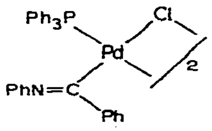

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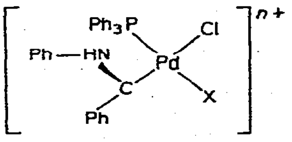
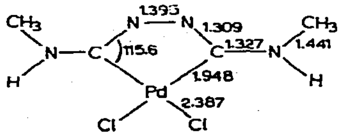


X = Cl, n = 0
X = PPh_3, n = 1

(31)

Analogs of Chugaev's salt, $[M(C_4H_8N_4R)(MeNC)_2]^+$ have been prepared for M = Pd; R = H; M = Pt, R = H, Me, Ph, $CONH_2$, and the isocyanide ligands have been displaced by a variety of neutral ligands[67,68]. Neutral complexes, $M(C_4H_{10}N_4)X_2$ (X = Cl, Br, I, CN) in which the carbene moiety is protonated have been obtained by reaction with mineral acid or by metathesis. The structure of one of these molecules, $(C_4H_{10}N_4)PdCl_2$, has been determined (32)[67,68].

A structural determination of (33) [obtained from the reaction of $(PEt_3PtCl_2)_2$ and (34)] has found the PtCNN plane of the heterocyclic carbene to lie at an angle of 70° from the metal coordination plane[69].



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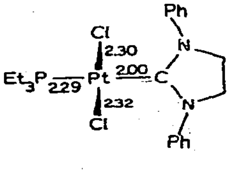

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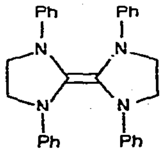


(34)

An unusual reagent, $Li[RCONi(CO)_3]$ has been used by Fukuoka et al. for the dimethylcarbamoylation or alkoxycarbonylation of organic halides in high yields for R = NMe_2 or O-t-Bu[70]. Reaction with R^1COCl gave R^1CONMe_2 (75–95%) and with Ph(CO)Ph gave on hydrolysis $PhCPh(OH)CONMe_2$ (30%).

III. METAL FULMINATES AND ISOCYANIDES

Beck has reviewed the field of metal fulminate chemistry[71], and has published a new route to $(PPh_3)_2Pt(CNO)_2$ by refluxing $(PPh_3)_4Pt$ in $EtOH/H_2O/C_6H_6/CH_3NO_2$ (1/1/1/3)[72].

The structure of Ni(PhN=NPh)(t-BuNC)$_2$ has been found to contain a π-bonded azobenzene with the NiCC plane at a dihedral angle of 1.2(3)° to the NiNN plane[73].

Preliminary descriptions of the structures of *cis*-$PtCl_2$(EtNC)(PEt_2Ph) and *cis*-$PtCl_2$(PhNC)$_2$ point out the equivalence of the Pt–C distances (1.89 Å) and note the small deviation from linearity in the RNC unit (172°; and 178 and 175° respectively)[74].

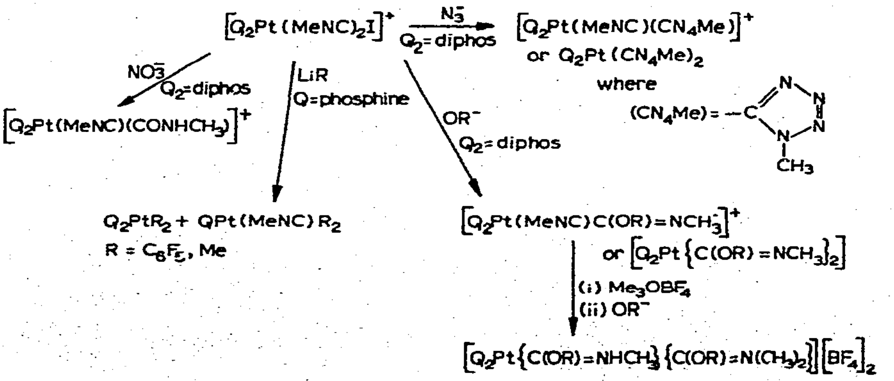
An infrared study on the ligand substitution of $(F_3P)_4M^0$ (M = Ni, Pt), by (c-C_6H_{11}NC) in n-alkane and toluene has concluded that the reactions are S_N1. Enthalpies of activation and thermal decomposition temperatures have been used to suggest that M–P bond strength in the complexes varies as Ni > Pd > Pt[75].

A diamagnetic palladium(I) dimer, $[(t\text{-BuNC})_2PdX]_2$ (X = Cl, Br, I) was reported as the product of Pd(t-BuNC)$_2$ and PdX_2(t-BuNC)$_2$ at –30° in C_6H_5Cl. Oxidative addition of $PhCH_2I$ to Pd(t-BuNC)$_2$ also have the species in the presence of t-BuNC. Attempts at bridge cleavage gave compounds of the type $[(PPh_3)Pd(t\text{-BuNC})I]_2$ and $[DiphosPdI]_2$[76]. These complexes are formally Pd^I and clearly worthy of a detailed investigation.

Displacement of C_2H_4 from $(PPh_3)_2PtC_2H_4$ by t-BuNC gives $(Ph_3P)_2$Pt(t-BuNC)$_2$. This complex will take up CO to give $(PPh_3)_2$Pt(t-BuNC)CO and will oxidatively add MeI, CF_3I and I_2 to yield salts formulated as $[(Ph_3P)_2Pt(t\text{-BuNC})_2R]I$[77].

Salt-like complexes, *trans*-$[PtQ_2(CNR)alkyl]I$ (Q = PPh_3, PMe_2Ph; R = C_6H_{11}, t-Bu), have been formed from the appropriate iodide complex by displacement with RNC. Refluxing the salts (alkyl = Me) in C_6H_6 results in a rearrangement to $Pt(PMe_2Ph)_2I$-$[C(Me)=NC_6H_{11}]$[78].

$[Me_3O]BF_4$ will methylate platinum(II) cyanides to give isocyanide complexes. Ligand substitution reactions on $(PR_3)_2PtX_2$ by MeNC yield a variety of cationic and neutral complexes depending on the nature of PR_3, X, and on the reaction conditions. Dealkyla-



Scheme 3. Reactions of cationic platinum isocyanides.

tion of a coordinated isocyanide has been observed for [DiphosPt(MeNC)X]X[79]. Heating this complex in C_6H_6 yields the cyanide complex with the loss of MeX. A wide range of anions have been substituted into cationic and neutral Diphos-platinum isocyanides with some of the reactions being outlined in Scheme 3[79].

Coordinated isocyanides are susceptible to nucleophilic attack by OH^-, SH^-, NHR^- to give complexes such as $(Ph_3P)_2Pt(MeNC)(CONHMe)^+$, $(Ph_3P)_2Pt(MeNC)(CSNHMe)^+$ and $(Ph_3P)_2Pt(MeNC)[C(NR)NHMe]^+$[80].

IV. METAL CYANIDES

The anions $M(CN)_4{}^{2-}$, M = Ni, Pd, have been determined structurally with different cations. The anions are square planar: Ni–C, 1.86 Å; C–N = 1.15 Å and Pd–C, 1.99 Å, C–N, 1.16 Å[81,82]. A crystallographic analysis for the complex anion $Rb_4[Ni_2(CN)_6]$ has also been reported[83]. Two five coordinated nickel complexes (5-alkyl-5H-dibenzo-phosphole) $Ni(CN)_2$, alkyl = Me, Et, have been analyzed by X-ray crystallography. Depending on the solvent from which it has been crystallized, the methyl compound has a tetragonal form or a trigonal bipyramidal form which is the form found for the ethyl analog[84].

A mechanism for the oxidative addition of Br_2 to $Pt(CN)_4{}^{2-}$ and $Pt(NH_3)_4{}^{2+}$ has been discussed with regard to kinetic studies[85]. Potentiometric equilibrium constants have been obtained for the substitution of bromide by H_2O in $(PtBr_2X_4)^n$ ($X = NH_3$, $n = 2+$; X = Cl, NO_2, CN, $n = 2-$)[86].

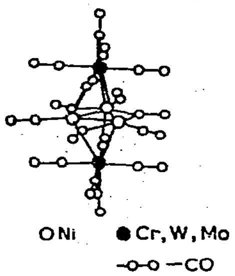
The oxidative addition of HCN to $Ni[Ph_2P(CH_2)_4PPh_2]_2$ yields $[Ni(CN)_2(Dpb)]_2$ and $Ni(CN)_2(Dpb)$[87].

Cyanogen will add to $M(Ph_2P(CH_2)_nPPh_2)_2$ (M = Ni, $n = 2, 3, 4$; M = Pd, $n = 2, 3$) and to $Pt(PPh_3)_4$ to give dicyanide complexes in a reaction which is far more rapid than the corresponding addition to $PtCl_2(PPr_3)_2$[88].

Replacement of Cd ions in the clathrate Cd-En-$[Ni(CN)_4]\cdot 2C_6H_6$ gave three new clathrate compounds with Ni, Cu and Zn[89].

V. METAL CARBONYLS

A novel reaction between $Ni(CO)_4$ and dinuclear metal decacarbonyl anions of Cr, Mo and W give transition metal atom cluster systems $[M_2Ni_3(CO)_{16}]^{2-}$-structure (35) (X-rays)[90].

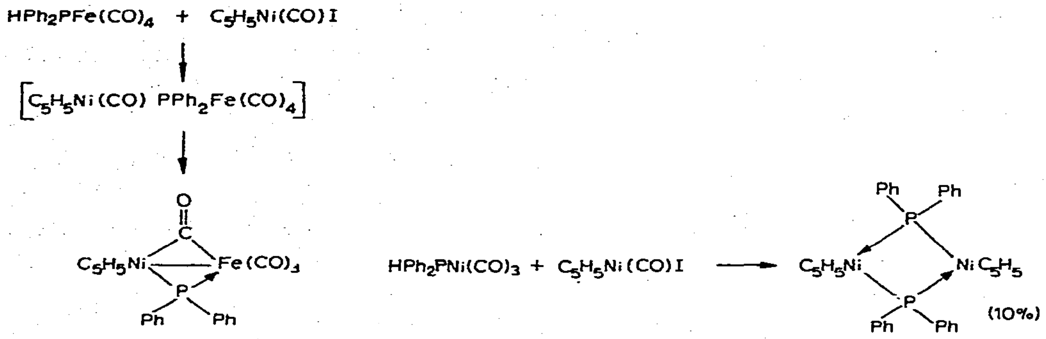


(35)

The infrared spectra for the series $Ni(CO)_n$, $n = 1$ to 4, has been recorded at 4°K in an argon matrix[91]. *Ab initio* calculation of the bonding in $Ni(CO)_4$ has been treated in a publication by Hillier and Saunders[92].

The complexes, $Ni(CO)_3L$, ($L = P\text{-}t\text{-}Bu_2F$, $P\text{-}t\text{-}BuF_2$) were prepared as part of a study on the ligand properties of L[93]. A study of the complexes of *cis*-1,2-bis(dimethylarsino)-ethylene included the complex $Ni(CO)_2L$[94]. The complex $Ni(CO)_2(Ph_2PCH_2CH_2)_2PPh$ was prepared as part of a series of syntheses using polydentate phosphines and it is reported to lose one CO on heating[95]. One or two CO units can be picked up with the loss of phosphine by $(PPh_3)_4Ni^0$ and by $Phos_2Ni^0$ ($Phos = Ph_2P(CH_2)_nPPh_2$; $n = 2$, 3 or 4). For $Phos_2Ni(CO)$ complexes, one unidentate Phos unit is proposed[96]. The phosphite complexes, $[(PhO)_3P]_3NiCO$ have been prepared from $Ni(Acac)_2 + P(OPh)_3 + AlEt_3 + CO$, or by addition of CO to $Ni[P(OPh)_3]_4$[97]. The former reaction can also be used to prepare dicarbonyl products[97].

Dehydrohalogenation of $HPh_2PM'(CO)_n$ ($M' = Fe$, $n = 4$; $M' = Ni$, $n = 3$) with metal halides in the presence of $HNEt_2$ has provided a route to dinuclear complexes of the type (36) and (37)[98].



(36) (37)

The ditertiary arsine ligands, ferrocene-1,1′-$(AsMe_2)_2$ (Fdma) and ferrocene-1,1′-$(AsPh_2)_2$ (Fdpa) formed complexes of the type $(Fdma)MX_2$ ($M = Pd$, $X = Cl$, Br; $M = Pt$, $X = Cl$, Br, I) but the analogous $M = Ni$ compounds could not be isolated[99]. The compound $LNi(CO)I_2$, $L = $ Fdma, Fdpa, was formed however from $LNi(CO)_2$ and I_2[99].

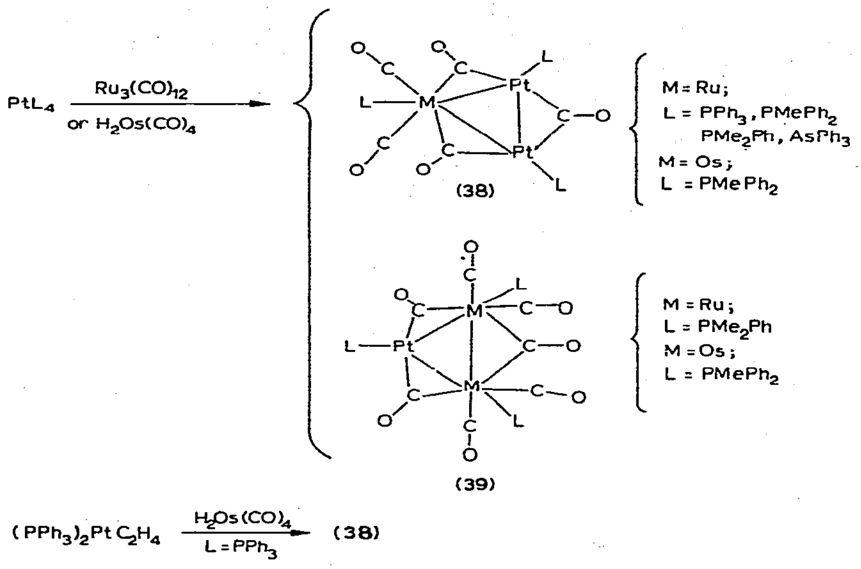
The dimer $[(PEt_3)_2PtCl]_2^{2+}$ has been found to yield *trans*-$[PtCl(CO)(PEt_3)_2]^+$ in reactions with C_2F_4 and H_2O or aldehydes and to cause the catalytic decomposition of formic acid[100].

Platinum halides heated in dimethylformanide give a solution containing carbonyl halide species. Addition of $N(alkyl)_4Cl$ gives $Pt(CO)Cl_3^-$; Bipy gives $COCl_2Pt(Bipy)PtCl_2CO$; and addition of HCl followed by Bipy gives $Pt(Bipy)COCl^+Pt(CO)Cl_3^-$ [101]. Dimeric platinum carbonyls, $COX_2Pt(NN)PtX_2CO$, can be prepared with bridging En or 4,4′-bipyridyl(NN) by displacing C_2H_4 or $Me_2C(OH)C{\equiv}CC(OH)Me_2$ from the π-organoplatinum dimer with CO. Detailed assignment of the infrared spectra of these complexes has been reported[102].

PtL_4 reacts with $Ru_3(CO)_{12}$ and $H_2Os(CO)_4$ to give platinum–carbonyl cluster compounds (38), (39)[103a].

The trinuclear cluster $[Pd_3(CO)_3(PPh_3)_3]$ has been obtained by treatment of equimolar quantities of $Pd(acac)_2$, and PPh_3 with CO in the presence of $AlEt_3$. The mononuclear complex $Pd(CO)(PPh_3)_3$ heated in ether gives an equilibrium with another cluster compound $[Pd_3(CO)_3(PPh_3)_4]$[32].

$Ni(CO)_4$ has been used synthetically in the carboxylation of methylenecyclobutane[103b], propene[103c], arylphenylpropenone[103d] and aryl halides[103e].



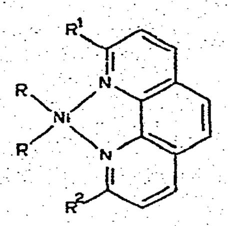
VI. FLUOROCARBON COMPLEXES

A full X-ray structural determination has been published for the mixed bis(aryl) nickel complex *trans*-$(PMePh_2)_2Ni(C_6F_5)(C_6Cl_5)$ (see AS '70, p. 209). The molecule is of C_2 symmetry with $Ni–C_6Cl_5$ (1.905(10) Å) shorter than $Ni–C_6F_5$ (1.978(10) Å)[104].

Decarboxylation of $(RCO_2)_2NiL$ ($R = C_6F_5$, *p*-$MeOC_6F_4$ or *p*-$EtOC_6F_4$; L = bipy, phen) has been used as a preparative route to fluorocarbon–nickel complexes[105]. The α-substituted Phen complexes (40) were separated (1–11% yield) as a minor side product.

The ^{19}F NMR spectra have been reported for the series of complexes $Pt(C_2F_4)L_2$ (L_2 = Bipy, Phen, 5-methyl-*o*-phenanthroline, Diphos; $L = PEt_2Ph, PMe_2Ph, PMePh_2$, $P\text{-}n\text{-}Bu_3$, PPh_3)[106].

Reaction of C_2F_4 or $CF_3C{\equiv}CCF_3$ with *trans*-$PtXCH_3L_2$ (X = halogen, L = phosphine, arsine, stibine) forms 1/1 complexes $PtXCH_3L_2{\cdot}C_2F_4$ and $PtXCH_3L_2{\cdot}C_4F_6$ (41). If the reaction with C_4F_6 is carried out in a sealed tube over several weeks rearrangement and

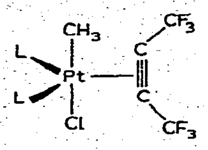


(40)

R = R¹ = p-MeOC$_6$F$_4$; R² = H

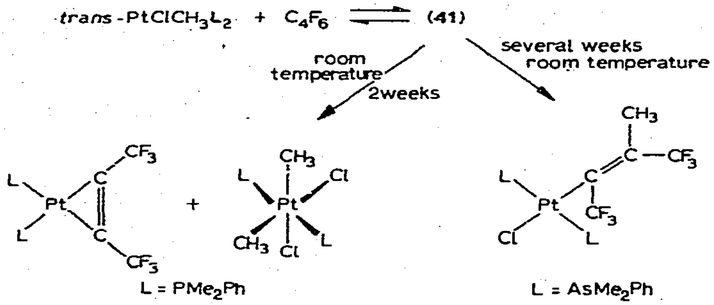
R = R¹ = R² = p-MeOC$_6$F$_4$

R = R¹ = p-EtOC$_6$F$_4$; R² = H



(41)

insertion take place (Scheme 4)[107]. Reaction of $L_4Pt^0 + C_4F_6$ gave compounds of the type $L_2PtC_4F_6$ ($L = PMePh_2, PMe_2Ph, PMe_2C_6F_5$)[108].

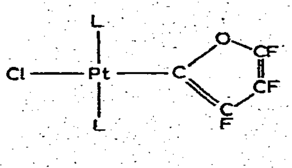


Scheme 4. Sealed tube reactions of (41).

Reaction of perfluoropropene and perfluorocyclobutene with *trans*-$PtHCl(PEt_3)_2$ in cyclohexane at 120° gave $PtCl(PEt_3)_2(CF{=}CFCF_3)$ and $PtCl(PEt_3)_2$(cyclo-C_4F_5). Reaction of these products with SiF_4/H_2O in C_6H_6 gave *trans*-$[PtCl(PEt_3)_2(CO)]SiF_5$ and $PtCl(PEt_3)_2(C_4F_3O)$ (42) (along with some *trans*-$[PtCl(PEt_3)_2(CO)]SiF_5$) respectively[109].

C_4F_6 reacts with $(COD)_2Ni$ to give $(COD)Ni[C_6(CF_3)_6]$ and $(COD)_2Ni_2[C_6(CF_3)_6]$. Displacement reactions on the monomeric complex yield $L_2Ni[C_6(CF_3)_6]$ ($L = PMePh_2$, $AsMe_2Ph$, PPh_3, $P(OMe)_3$, $P(OCH_2)_3CMe$)[110]. C_4F_6 with $Ni(AsMe_2Ph)_4$ gives the same product while the PPh_3 complex can also be reached by direct reaction of $C_6(CF_3)_6$ with $(Ph_3P)_2NiC_2H_4$. The binuclear product reacts with $L = P(OCH_2)_3CMe$ to give L_4Ni_2-$[C_6(CF_3)_6]$ (43) which has been described as fluxional in the NMR[110].

cis-Platinum acetylides result from the addition of $CF_3C{\equiv}CH$ or $CF_3CF_2C{\equiv}CH$ to $Pt(PPh_3)_4$ while $CF_3C{\equiv}CCF_3$ forms a π-complex[111].



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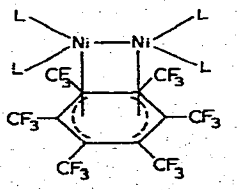
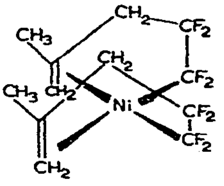


(43)

Treatment of L_4Ni^0 (L = $AsMe_2Ph$, o-$(AsMe_2)_2C_6H_4$) with C_2F_4 and C_2F_3H results in the isolation of the chelate compounds, $L_2\overline{NiCF_2CF_2CF_2CF_2}$ and $L_2\overline{NiCF_2CFHCFHCF_2}$. The halides C_2F_3X, (X = Cl, Br), CF_2CCl_2 and CFClCFCl oxidatively add to form vinyl-chloro or -bromo complexes when treated with the above Ni^0 species, Pd(t-BuNC)$_2$ or L_4Pd^0 (L = $AsMe_2Ph$)^{112,113}. C_4F_6 gives the cyclic olefin complex $(AsMe_2Ph)_2\overline{NiCF_2CF{=}CFCF_2}$. With bis(2-methylallyl)nickel, C_2F_4 gives purple red crystals for which the molecular structure (44) has been proposed. The complex $[o\text{-}(AsMe_2)_2C_6H_4]\overline{Ni(CF_3)_2CO}$ reacts with $(CF_3)_2CO$ or $(CF_3)_2CNH$ to give a five-membered insertion product (45)^{112}. Pd(t-BuNC)$_2$ and $(AsMe_2Ph)_4Pd^0$ also give this type of insertion product with $(CF_3)_2C{=}X$ (X = NH, O), whereas $(PPh_3)_4Pd^0$ gives $(PPh_3)_2\overline{PdC(CF_3)_2NH}$^{114}.

Direct reaction of $(CF_3)_2C{=}X$ with (t-BuNC)$_4$Ni^0 gives (t-BuNC)$_2\overline{NiC(CF_3)_2{\cdot}X{\cdot}C(CF_3)_2X}$ (X = NH, O) as for the analogous palladium compounds^{112,113}. Another route to these five-membered ring systems is by insertion of ketone or imine into (t-BuNC)$_2\overline{NiC(CF_3)_2X}$ (X = O, NH). In the case of imine insertion into the X = O compound the product is (t-BuNC)$_2\overline{NiC(CF_3)_2NHC(CF_3)_2O}$ (47) only, whereas the combination of ketone and X = NH gives two different insertion products. If PhNC is used, reaction with the ketone leads to (PhNC)$_2\overline{NiC(CF_3)_2O}$ which can then insert imine^{114}. C_2F_4, C_4F_6 in reaction with (t-BuNC)$_4$Ni^0 form (t-BuNC)$_2\overline{NiCF_2CF_2CF_2CF_2}$ and (t-BuNC)$_2\overline{NiCF_2CF{=}CFCF_2}$ whereas $(CN)_2C{=}C(CF_3)_2$ or $CF_3CF{=}CF_2$ yield (t-BuCN)$_2\overline{NiC(CF_3)_2C(CN)_2}$ and (t-BuNC)$_2\overline{NiCF_2CFCF_3}$^{114}. The analogous palladium compounds have also been prepared^{113}. Addition of $C(CF_3)_2CO$ to (t-BuNC)$_2$NiO$_2$ gives an unusual ring system, (t-BuNC)$_2$-$\overline{NiOOC(CF_3)_2O}$ which readily loses 1/2 O_2 in Et_2O to give a four-membered ring compound (t-BuNC)$_2\overline{NiOC(CF_3)_2O}$.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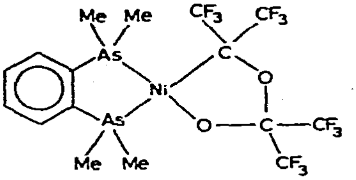
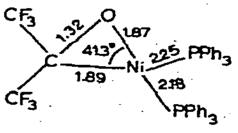

(45)

On the basis of all the above reactions, it is clear that activation of $(CF_3)_2C{=}X$ toward reaction with another electronegatively substituted unsaturated molecule occurs on nickel complex formation^{112,113,114}.

Preliminary X-ray crystallographic data have been reported for a three-membered ring compound, $(Ph_3P)_2\overline{NiC(CF_3)_2O}$ (46) and a five-membered ring compound, (t-BuNC)$_2$-$\overline{NiC(CF_3)_2NHC(CF_3)_2O}$ (47)^{115}.



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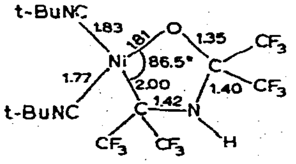
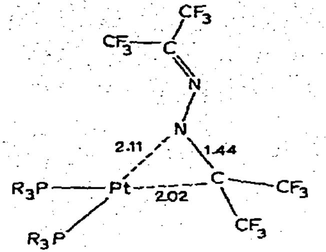


(47)

$(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$ on reaction with M^0 compounds affords the complexes $L_2\overline{M(CF_3)_2C{=}N}{-}N{=}C(CF_3)_2$ ($M = Ni$, $L_2 = COD$, $L = t\text{-}BuNC$, PPh_3; $M = Pd$, $L = t\text{-}BuNC$, $C_6H_{11}NC$ and $M = Pt$, $L = PPh_3$) which have a square planar structure (48)[116].

The lithium reagent $(CF_3)_2C{=}N{-}Li$, (RLi), and the appropriate metal chloride have been used to generate the ketenimides, *cis*-$(PPh_3)_2PtRCl$, *trans*-$(PMe_2Ph)_2Pt(R)H$, *cis*-$(PMe_2Ph)_2Pt(R)Cl$, *cis*-$(PMe_2Ph)_2PtR_2$ and *trans*-$(PPh_3)_2Pt(R)H$ ($R = (CF_3)_2\,C{=}N{-}$). The last complex isomerizes in the presence of phosphine to give (49)[117].



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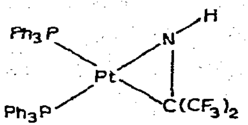


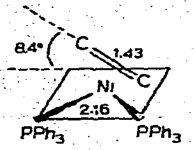
(49)

VII. OLEFIN AND ACETYLENE COMPLEXES

Monoolefin and acetylene complexes of nickel, palladium and platinum have been reviewed by Jonassen and Nelson (230 references)[118]. The role of this type of complex in catalysis is discussed in a review of π-complex intermediates in catalytic exchange reactions[119]. Theoretical treatments of cycloaddition reactions carried out with olefin–transition metal catalysts have also received attention[120,121].

A great deal of work has been published on the chemistry of species $L_2M(\pi\text{-}R)$. Structural determinations where $\pi\text{-}R = ClFC{=}CF_2$, $Cl_2C{=}CF_2$, $Cl_2C{=}CCl_2$[122] and $Cl_2C{=}C(CN)_2$[123]; $L = PPh_3$; $M = Pt$, have been reported. For the last complex, Pt–C (of $=CCl_2$) (2.00(2) Å) is shorter than Pt–C (of $=C(CN)_2$) (2.10(2) Å) and the CN groups are bent back further (69.9 ± 3.3°) than the chlorides (48.4 ± 2.3°). In all cases the ethylene units lie very close to coplanar with the PtPP plane.

In $(Ph_3P)_2Ni(C_2H_4)$ the C=C bond is twisted out of the plane by 8.4°[124] (50). In



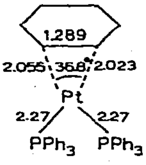
(50) Ni—C, 1.99

$(Ph_3P)_2Pt(C_2H_4)$ the out-of-plane twist is only 1.3°. Evidence from the NMR of these complexes in toluene indicates C_2H_4 dissociation for M = Pt but not for M = Ni, although exchange of free and coordinated ethylene will occur in the presence of excess olefin,

(E_a = 11.7 kcal/mole). An associative mechanism has been proposed for reactions of the type $L_2Pt(\pi\text{-}R)$ + acetylene$^1 \rightleftharpoons L_2Pt(\text{acetylene}^1)$ + R, where R is an acetylene or olefin[125,126]. Cook and co-workers have also presented ESCA* data for a series of low valent platinum complexes $(PPh_3)_2PtL$. They found that the trend of binding energies for Pt 4f 7/2 electrons correlate reasonably with the expected trend in the degree of metal oxidation, *i.e.* L = $(PPh_3)_2 < PhC{\equiv}CPh \sim H_2C{=}CH_2 < CS_2 < O_2 < (Cl)_2$. The values of oxidation state of platinum being taken as 0 for $(PPh_3)_2$ and 2 for $(Cl)_2$ respectively, the other ligands correspond to 0.7($PhC{\equiv}CPh$), 0.8($H_2C{=}CH_2$), 1.3(CS_2), and 1.8(O_2)[127].

Reduction of $Pd(Acac)_2$ with $AlEt_2(OEt)$ in Et_2O in the presence of C_2H_4 and L has resulted in the isolation of $L_2PdC_2H_4$ (L = PPh_3, $P(\text{cyclo-}C_6H_{11})_3$ and $P(o\text{-tolyl})_3$). The loss of ethylene can lead to $Pd[P(\text{cyclo-}C_6H_{11})_3]_2$[128].

X-ray analysis has led to the structures (51), (52), (53) for π-bonded cyclohexyne (51)[129], cycloheptyne (52)[130] and 1,2-dimethylcyclopropene (53)[131]. In (53) the methyls are bent out of the ring plane, the angle between (MeC=CMe) and (ring) is 112°. Treatment of (52) with $HOOCCF_3$ gives the σ-cycloheptenyl derivative $[(\sigma\text{-cycloheptenyl})(OOCCF_3)Pt(PPh_3)_2]$[130].



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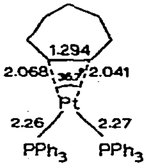

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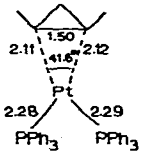
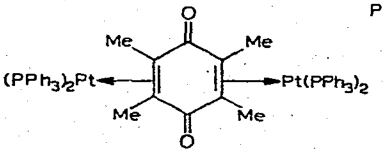


(53)

Spectral studies on a series of complexes $(PPh_3)_2PtL$ (L = $CH_2{=}C(CN)H$, $CH_2{=}C(Ph)H$, $(CO_2Me)HC{=}CH(CO_2Me)$, maleic anhydride, $CH_2 = CHAc$, $CH_3(H)C = CHCHO$, $PhHC = CH(CO_2Et)$, $AcOC \equiv COAc$ and $PhC \equiv CAc$) have supported the hypothesis that the presence of electronegative substituents increases the interaction between the metal and ligand[132]. A similar conclusion has been reached for a series of compounds where L is a quinone[133]. Several fashions of bonding have been observed in these complexes. *para*-Quinones are symmetrically bound presumably via both double bonds. For duroquinone structure (54) has been proposed and (55) represents the oxidative addition product obtained for chloranil[133]. *ortho*-Quinones are thought to coordinate via the carbonyl oxygens on the basis of IR and NMR data, *i.e.* (56)[133]. These compounds have been compared to



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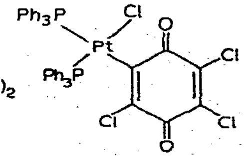

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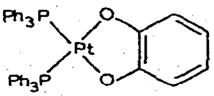

(56)

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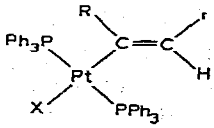
*ESCA = electron spectroscopy for chemical analysis.

the related $M(NO)(PPh_3)_2L$ complexes for M = Co, Rh, and Ir where L is an activated acetylene or quinone[134].

$(PPh_3)_2Pd(NC{-}C{\equiv}C{-}CN)$ has been prepared by displacement of fumaronitrile from $(PPh_3)_2Pd(C_4N_2H_2)$ with $NCC{\equiv}CCN$[135]. From studies of the equilibrium Ni(Bipy)(solvent) + olefin ⇌ Ni(Bipy)olefin + solvent. A set of stability constants for a variety of olefin complexes has been obtained[136]. The π-acceptor ability of the olefin was found to be an important factor in the formation of a stable complex with the stability constants showing a linear correlation with the energy of the π^* orbitals (as estimated from the ionization potentials and π to π^* excitation energy of the olefin) and also with the Alfrey-Price e values which are indicative of the polarity or electron density of the vinyl group. The stability constants for $R_2Ni(Bipy)(olefin)$ (R = Me, Et, n-Pr, i-Bu) were measured visually and some correlation was observed with the specific rate constants of the reaction of $R_2Ni(Bipy)$ with olefin at 30°[136].

Some difference was noted in the chemistry of $(Ph_2P(CH_2)_nPPh_2)_2Ni^0$, depending on whether $n = 4$ (Dpb) or $n = 3$ (Dpp). Reactivity towards a variety of olefins and acetylenes was found to be $Ni(Dpb)_2 > Ni(Dpp)_2$[137]. Polymerization of and reaction with acetylene was noted for both compounds. $(CN)_2C{=}C(CN)_2$ reacted with both to give complexes such as $(CN)_2C{=}C(CN)_2Ni(Dpb)$[137].

Reaction of $(PPh_3)_2Pt(CH_3C{\equiv}CCH_3)$ with HX (X = Cl, Br. HCOO, CF_3COO, CH_3COS, C_6H_5COS and picrate) gives $(PPh_3)_2PtX_2$ and an isomeric mixture of *cis-* and *trans*-2-butenes (*cis* predominating)[138]. A greater yield of *trans*-butenes is favoured by sulfur containing HX and by the presence of thiophene, allylmethyl sulfide or aniline. A mechanism for the decomposition via Pt^{II} and Pt^{IV} hydrides (from the oxidative addition of HX) and an isolable vinyl intermediate (57) has been postulated[138].

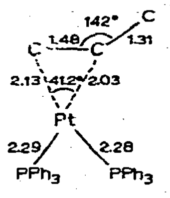


(57)

π-Olefin nickel complexes, $(PR_3)_2NiPhHC{=}CHPh$ (R = Ph, Bu) were obtained by displacement of azobenzene from $(PhNNPh)Ni(PR_3)_2$ or directly from Li/THF reduction of $(R_3P)_2NiCl_2$ with stilbene[139]. The isocyanides $(t\text{-}BuNC)_2MR$ (M = Ni, Pd) have also been reported for R = azobenzene, $(CN)_2C{=}C(CN)_2$, $(MeOOC)C{\equiv}C(COOMe)$, $PhC{\equiv}CPh$, fumaronitrile, dimethylmaleate and maleic anhydride[140,141].

Activated olefin complexes of stoichiometries $(t\text{-}BuNC)_3ML$ or $(t\text{-}BuNC)_2ML_2$ (M = Ni, Pd) have been prepared[141]. The two stretching frequencies of the isocyanide ν_A, ν_b show a linear correlation with the electron affinity of the olefin as does the quantity $(\nu_A - \nu_b)$. The authors have proposed the use of $(\nu_A - \nu_b)$ as a measure of the effective back bonding of the olefin[141]. Reaction of $(PhNC)_2Pd(CN)_2C{=}C(CN)_2$ with PPh_3 or $AsPh_3$ yields $Pd(PhNC)(EPh_3)(olefin)$[142]. The reaction with two phosphites or Diphos displaced both isocyanide ligands.

The structures of a Pt^0- and a Pt^{II}-allene complex have been reported with allene in the coordination plane (58)[143] and perpendicular to it (59)[144] respectively.



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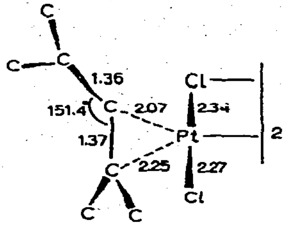

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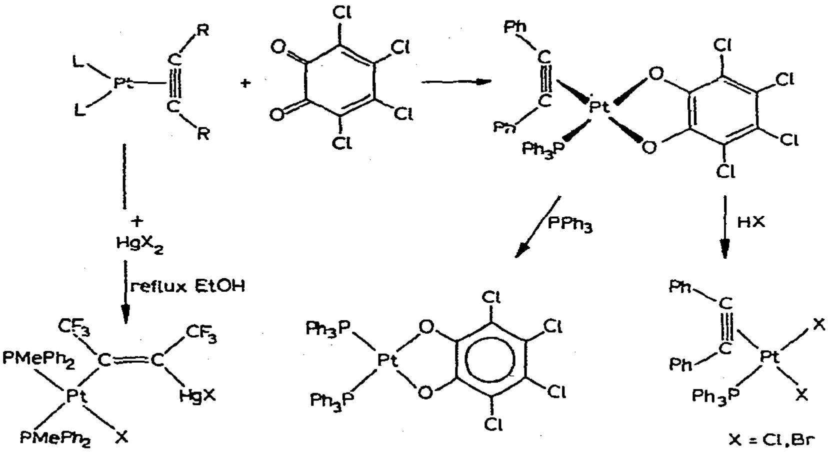
A high resolution NMR study on a series of complexes $(PPh_3)_2PtL$ (L = terminal acetylenic and methylacetylenic alcohols)[145] has been published. The complexes have been found to be planar in solution with dissociation occurring for the methylacetylenic alcohols. In $CDCl_3$, these complexes appear to undergo an irreversible oxidative addition with the solvent since the amount of free ligand is not the same before and after temperature variation. The product of this reaction has been formulated as $(Ph_3P)_2PtCl(CDCl_2)$[145].

Scheme 5 describes the chemistry of $(PR'_3)_2Pt(RC{\equiv}CR)$ with tetrachloro-*o*-quinone and mercury halides[146].



Scheme 5. Reactions of platinum–acetylene complexes.

Admission of olefins to a system in which Pt was supported on silica gave rise to ultraviolet absorption bands at 270 and 310 nm which disappeared on hydrogenation[147]. Admission of acetylene gave rise to these bands only when hydrogen was simultaneously introduced. The bands have been assigned to the charge-transfer bands of a coordinated olefin of the type observed in $Pt(PPh_3)_2C_2H_4$ and Zeise's salt[147].

The inertness of platinum metal depends on its physical state since while bulk metal is unreactive, metal vapour will react with a variety of unsaturated substrates condensing at $-196°$[148]. Reaction was noted with propene, 1-butene, 1,3-butadiene, allyl chloride, and COD by analysis of the products obtained[148].

Several investigations on the nature and chemistry of Zeise's salt have appeared in 1971. A redetermination of the crystal structure by Jarvis *et al.* differed from previous work principally in the nature of the potassium coordination polyhedra[149]. A SCF—MO treatment was undertaken by Kato and used to assign the ultraviolet spectrum[150]. Zeise's salt was formed in low yield by a new preparative route from Na_2PtCl_4, $N(n\text{-}Bu)_4Cl$, and EtOH at room temperature[151]. Adamson has elucidated the photochemistry of Zeise's salt[152]. A ^{35}Cl NQR study has assigned the lowest NQR frequency (16.0001 MHz) to *trans*-Cl, and the two higher frequencies (20.134, 20.370 MHz) to *cis*-Cl in Zeise's salt[153]. Comparison with other olefin platinum(II) anions and neutral dieneplatinum chlorides has also been made[153]. ^{13}C NMR studies on a variety of organotransition metal complexes included Zeise's salt[154].

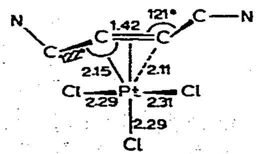
Formation constants for the related complexes $C_2H_4PdCl_3^-$, $C_2H_4PdCl_2 \cdot H_2O$ have been measured potentiometrically for the C_2H_4 + aqueous $PdCl_4^{2-}$ system[155].

The molecular core binding energies of a given *cis*/*trans*-isomer pair, L_2MX_2 (M = Pd, Pt; L = PR_3, $Me(H)C{=}CH_2$; X = halogen) (obtained from photoelectron spectroscopy studies), show that the binding energy in the metal is the same but that the binding energy of the halide is considerably lower in the *cis*-isomer (a change expected on the basis of previous metal—halide bond distances and ^{35}Cl NQR data)[156].

Comparison of metal—olefin stretching frequencies for $[Cl_2M\ \text{olefin}]_2$ have been related to the order of coordination strengths with the conclusions: Pd < Pt; vinylalcohol ~ vinyl ether ~ C_2H_4 (for M = Pt); propenyl ether > vinyl ether; and 2,2,2-trifluorovinyl ether ≫ alkyl vinyl ether[157]. A normal coordinate analysis of coordinated vinyl alcohol has led to the suggestion that the high C—O force constant indicates the contribution of a resonance structure $\bar{C}H_2{-}CH{=}\overset{+}{O}H$ in the complex[157].

The structures of $[(\pi\text{-}trans\text{-}2\text{-buten-}1,4\text{-diammonium})PtCl_3]Cl$[158] and $(PPh_4)[(\pi\text{-}cis\text{-}2\text{-buten-}1,4\text{-diol})PtCl_3]$[159], (60) and (61) respectively, have been reported.

The 1/1 adduct of $(CN)_2C{=}C(CN)_2$ and *trans*-$PtXCH_3L_2$ (L = AsR_3, PR_3) has been isolated and characterized as a formally six-coordinate species[160].



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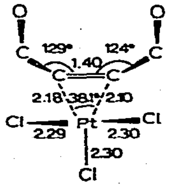
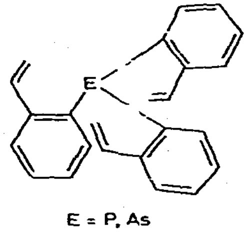


(61)

A complex formulated as $Cl_2Pt[HC{\equiv}CC(CH_3)_3] \cdot (CH_3)_2CHOH$ has been isolated during a study of the hydrosilation of the acetylene in i-PrOH by $H_2PtCl_6 \cdot 6H_2O$[161].

The positions of the protons relative to the metal in *trans*-$Cl_2PtPy(CH_2{=}CHR)$ (R = Me, i-Pr, t-Bu), have been discussed on the basis of NMR spectroscopy[162].

The ligands (62) form derivatives $PtBr_2$(ligand) in which the ligand coordinates as a chelate via an olefin and the Group VA donor[163]. Facile exchange occurs between the coordinated and two free olefins in solution as observed in the ^{1}H NMR. Bromination with 2 moles of Br_2 per complex saturates the free double bonds to yield (63). A similar set of ligands $CH_2{=}CH(CH_2)_nPPh_2$ (n = 1, 2, 3) have been treated with $(PhCN)_2PdCl_2$ and $PtCl_2$. Chelation is possible for n = 2, M = Pd, Pt; n = 3, M = Pt only. Nucleophilic attack on the products results in addition at the β carbon to give dimeric complex (64) which can undergo bridge cleavage reactions[164]. A bidentate ligand, complexing through one sulfur and one olefin, has been observed in the complexes $PdLCl_2$ and $PtLCl_2$ (L = *o*-alkyl-*N*-allylthiocarbamate)[165]. This structure has been confirmed by X-ray crystallography for $Pd[C_3H_5{\cdot}NH{\cdot}C(OMe)S]Cl_2$[166] (65).



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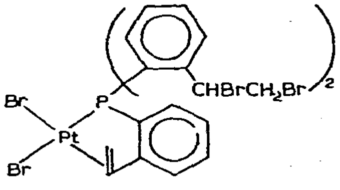
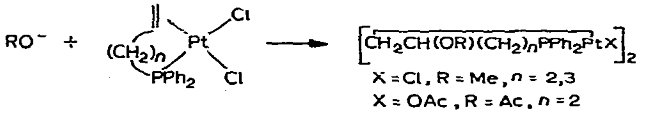


(63)

Optical activity in olefin–metal complexes has been reviewed[167] and has been the



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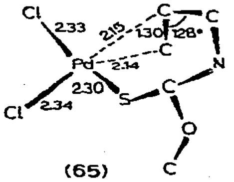

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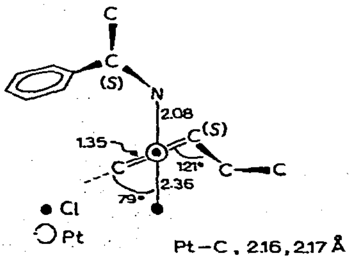

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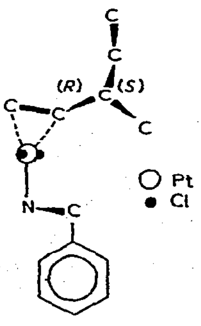
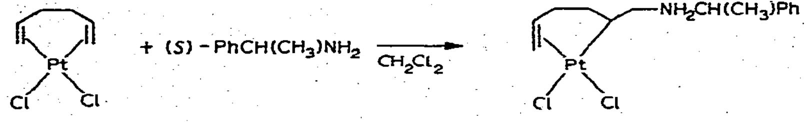


(67)

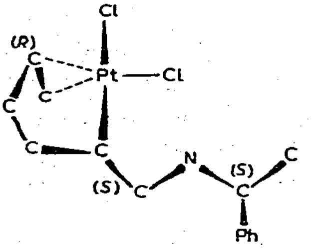
theme of several research papers. Structural studies have assigned the absolute configuration of (+)-*cis*-dichloro((*S*)-1-butene)((*S*)-α-methylbenzylamine)-platinum(II)[168] (66) and *trans*-dichloro ((2*R*, 3*S*)-3-methyl-1-pentene)(benzylamine)platinum(II)[169] (67).

Paiaro *et al.* have described the formation of a complex (68) which can be isolated as one or two diastereomers depending on whether it is precipitated slowly or quickly from the reaction mixture[170].

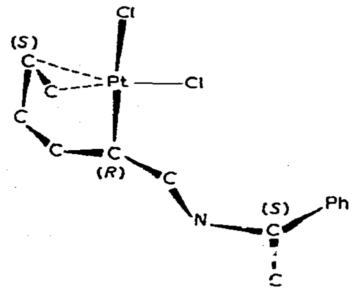


(68)

The racemic mixture of the diastereomers (+ and –) of (68) can be dimerized with base (Na_2CO_3) to give the dimers (+,+) and (–,–) which can be fractionally crystallized. The electronic spectra and circular dischroism spectra are reported[170]. The absolute configurations of the two diastereomers of (68) have been determined as (69a) and (69b)[171].



(69a)

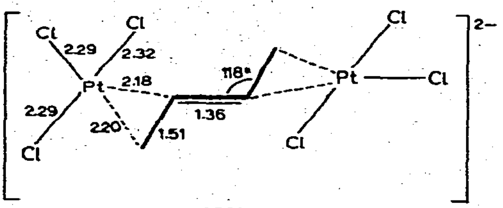


(69b)

Seven PtCl((*L*)-prolinato)(olefin) complexes have been isolated as diastereomers by crystallization and assignment of the absolute configuration. The rate of racemization has been determined by circular dichroism with the rate being related to the strength of the olefin–metal bond (styrene > propene > *trans*-2-butene > 2-methyl-2-butene)[172]. A quadrant rule for the assignment of stereochemistry on the basis of the *d*–*d* transitions in the circular dichroism spectrum of platinum(II) olefin complexes has been developed by Wrixon and Scott[173].

An unusual planar *trans*-butadiene bridge has been revealed in the structure determination of $(NMe_3Et)_2[Pt_2Cl_6(C_4H_6)]$ (70). The olefin makes an angle of 81° with the coordination plane[174]. A neutral DMSO derivative of this complex has been reported[175].

Abstraction of chloride from [1-(1-chloroalkyl)-π-allyl)] or hydride from (1-alkyl-π-allyl)PdCl/2 by strong acid or SbF_5 gives a species identified by Kramer and Lucas from NMR data as a cationic [*tetrahapto*-butadiene] palladium chloride complex which on reaction with base gives [(hydroxyalkyl)-π-allyl] PdCl/2 [176].



(70)

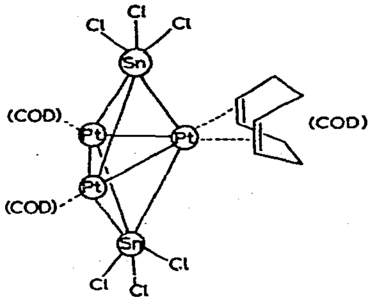
A bidentate butadiene (and cyclopentadiene) complex has been isolated with $Ni(P(OC_6H_4\text{-}o\text{-}C_6H_5)_3)_2$ at low temperature or from the thermal rearrangement of L_2Ni-(methylenecyclopropane)[177].

The interaction of 1,5-hexadiene $PtBr_2$ and TlAcac to yield $Pt_2(Acac)_4$(1,5-hexadiene) has been described by White[178].

An unstable species isolated as a by-product in the $Pd(OAc)_2$ catalyzed auto-oxidation of 1,4-cyclohexadiene has been formulated as a palladium(I) complex $[Pd_2(C_6H_8)(OAc)_2 \cdot \frac{1}{2}HOAc]$ on the basis of elemental analysis and chemical reactivity[179].

The preparation of COD derivatives of platinum(II) halide have been described in detail[180].

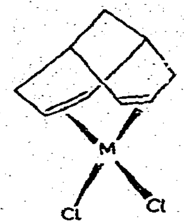
Vibrational infrared and Raman studies have been developed into an evaluation of force constants for the Pt–Sn cluster compound (71). In particular, the Pt–Pt force constant (1.36 mdyn/Å) is of interest as it is somewhat lower than that expected for a normal Pt–Pt single bond[181].



(71)

Because of the interest in 1,4-COD complexes as intermediates in isomerization and rearrangement reactions a broad range of transition metal complexes have been reacted with 1,4-COD to give products containing both 1,4- and 1,5-COD. Of special note, $Pd(PhCN)_2Cl_2$ and K_2PtCl_4 react to give Pd(1,4-COD)Cl_2 and Pt(1,5-COD)Cl_2[182]. The diene MCl_2 complexes, (72), (73) and (74), have been synthesized and characterized[183,184,185].

Reaction of hexamethyl Dewar benzene with $(C_2H_4)PtCl_2/_2$ gives (75)[186]. In acid conditions however the reaction with $PtCl_4^{2-}$ results in the formation of a cyclopentadiene complex (76) which may also be obtained from $PtCl_4^{2-}$ and C_5Me_5CHXMe (X = H, Cl,



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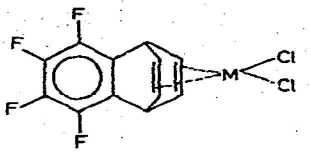

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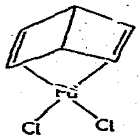

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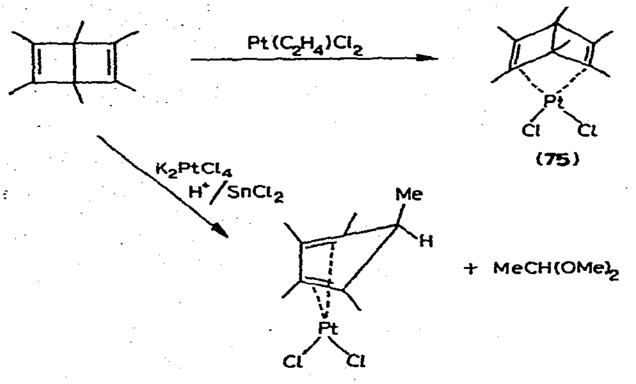
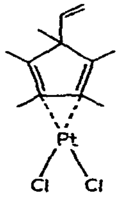
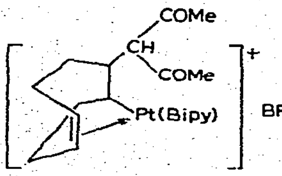




(77)

OMe, OEt) in acidic MeOH. This latter reaction with $(C_2H_4)PtCl_2/_2$ results in a mixture of (76) and (77). Complex (77) may be formed directly from the appropriate cyclopentadiene and $(C_2H_4)PtCl_2/_2$. Complex (77) which has an *endo* vinyl substituent can be isomerized to the *exo* analog by an unusual hydrogen catalyzed reaction[186]. The complexes $Pd(C_5Me_5Y)Cl_2$ have been assigned a stereochemistry on the basis of NMR with Y being *exo* with respect to palladium for Y = Et, CHClMe, CH(OR)Me and *endo* for Y = H[187]. A complex containing two enyl units and of stoichiometry $Pt(C_9H_9)_2$, has been prepared from excess *o*-allylphenyl Grignard and PtX_2[189]. Reaction of $Pt(C_9H_9)_2$ with 2HCl, $2PPh_3$, or 2CO gives the derivatives $(\pi\text{-}C_9H_{10})PtCl_2$, $(\sigma\text{-}C_9H_9)_2Pt(PPh_3)_2$ and *cis*-$(\sigma\text{-}C_9H_9)_2Pt(CO)_2$. The phosphine derivative will oxidatively add Br_2 or Cl_2 and the dicarbonyl on standing in benzene develops a ketonic CO stretch[189]. $[(COD)Pt(Acac)]BF_4$ may be forced to the enyl system (79) by the addition of Bipy[190].

Treatment of norbornadiene metal halides with AgOOCR has produced the carboxylate bridged complexes (80) (M = Pd, Pt)[191,192]. Both the ester and bridging OCCR will ex-



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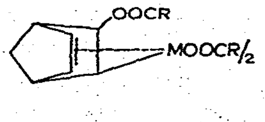

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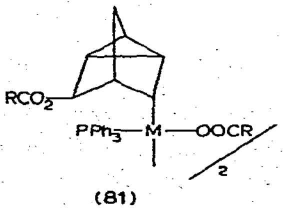


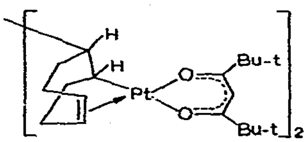
(81)

change with free HOOCR but by independent mechanisms[191]. Addition of PPh_3 to the dimeric norbornadiene system (80) generates a nortricyclene system $[(RCO_2C_7H_8)M(O_2CR)PPh_3]_2$ (81)[192]. White has reported that K_2PdCl_4, COD, and Br^- in basic aqueous solution will yield $[(2\text{-hydroxy-5-cyclooctenyl})PdBr]_2$[193]. Treatment of preformed $[(COD)(t\text{-}Bu(CO)CH(CO)Bu\text{-}t)M]BF_4$ with aqueous base will give (2-hydroxy-5-cyclooctenyl) complexes for M = Pd, Pt with an additional product, identified as (82), being formed for the M = Pt reaction[193].

Elimination of AgCl from $NBDPtX_2$ on reaction with $AgSCF_3$ generates $NBDPt(SCF_3)_2$[194]. With the palladium complex addition of SCF_3 to NBD also takes place to give two yellow crystalline products $[(C_7H_8SCF_3)PdCl]_2$ and $[(C_7H_8SCF_3)Pd]_2Cl(SCF_3)$ which by NMR have been assigned the nortricyclyl structures (83)[194].

The enyl complex $(C_{10}H_{12}OMe)PtPhL$ (L = Py, PPh_3; $C_{10}H_{12}$ = dicyclopentadienyl) has been obtained by reaction of the chloride analog with LiPh[195].

Wilke *et al.* have treated olefins with 1,5,9-dodecatrienenickel(0)L to give $(olefin)_2NiL$ (L = $P(cyclo\text{-}C_6H_{11})_3$, olefin = C_2H_4, $CH_2{=}CHCH_3$, 3-vinylcyclohexene, divinylcyclobutane, butadiene; and L = PPh_3, olefin = C_2H_4)[196]. The dibutadiene and divinylcyclobutane complexes both decompose with excess PPh_3 at +80° to give butadiene and its dimers. With CO at −78° both complexes give vinylcyclohexene[196]. From the chemistry and spectral data, a common species for both complexes in solution has been described as (84)[197a]



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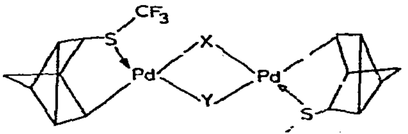
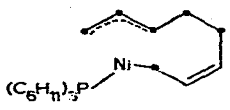


X = Y = Cl
X = Cl ; Y = SCF_3

(83)



(84)

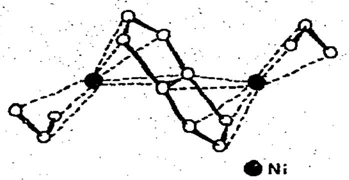
This complex has been isolated from the reaction of $[P(cyclo\text{-}C_6H_{11})_3]_4Ni_2(N_2)$ with butadiene by Brown *et al.* who suggest that it is formed not only in solution but retains this form in the solid state[197b].

Treatment of $(PPh_3)_2NiC_2H_4$ with boron halides displaces the ethylene to give a variety of phosphine nickel halides and in the case of BPh_2Br, a phosphine boryl nickel complex with bridging (BPh_2) groups[198].

In recent work, decomposition of the complexes $C_{18}H_{30}PdCl_2$ and $C_{18}H_{30}PdClBr$ (obtained from the reaction of di-t-butylacetylene with $(PhCN)_2PdCl_2$) using H_2 and Br_2 have given what are now established to be fulvene derivatives on the basis of the chemical and structural properties of the decomposition products[199].

VIII. ALLYL COMPLEXES

Structural determinations on allyl complexes included the centrosymmetric product (85) of the reaction of allyl $NiCl/2$ with dihydropentalenylenedilithium[200]. Broadbent and Pringle have confirmed the structure of $[(C_6H_8Cl)PdCl]_2$ (86) to be as suggested by Schultz[201]. The insertion product of cyclohexanone oxime into the $(\pi\text{-allyl-PdCl})_2$ binding system has been determined to be as in (87)[202].



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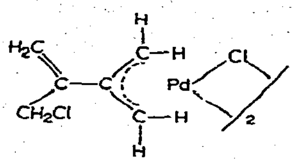

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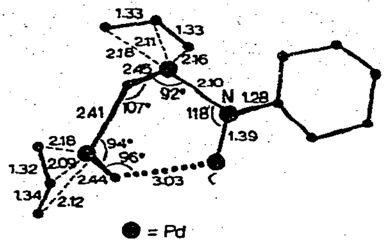


(87)

SCC-MO treatment of metal–allyl complexes indicate that metal–carbon overlap populations for bis(π-allyl) metal compounds lie in the sequence Ni ~ Pd < Pt and in the sequence Ni < Pd < Pt for the halide dimer[203]. A major conclusion of the work is that the π-allyl functions almost exclusively as an electron donor[203].

The enthalpies of formation of crystalline (−107.6 ± 1.7 kJ/mole) and gaseous (+18 ± 2.5 kJ/mole) $\pi\text{-allylPdCl}/_2$ have been determined by differential scanning calorimetry[204]. The bond dissociation energy for the palladium–allyl bond is > 237 kJ/mole[204].

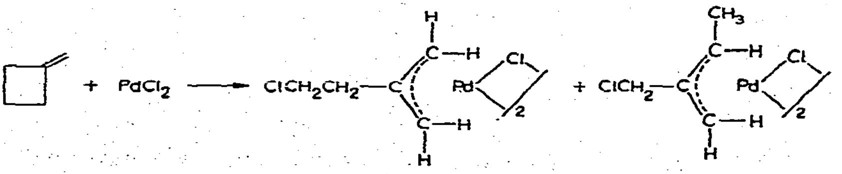
The activity of PPh_3 or DMSO as a bridge cleavage reagent for $\pi\text{-allylPdCl}/_2$ has been confirmed by a laser Raman study[205]. ^{13}C NMR data for a series of π-allylic complexes have been reported[206]. The mass spectral fragmentation patterns for a series of π-allylic palladium halides[207] and the equilibrium constants for $\pi\text{-allylPdCl}/_2$ in aqueous solution over a range of pH's have been published[208].

π-Allyl metal complexes may be prepared from the metal salts by several methods.

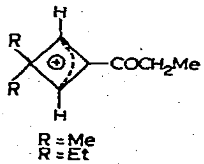
The interaction of olefins with $PdCl_2$ to yield $[\pi\text{-allylPdCl}]_2$ species is favoured under mild conditions when dimethylformamide (DMF) is the solvent[209]. The formation of $[(DMF)_2H]_2^+[Pd_2Cl_6]^{2-}$ occurs simultaneously and the role of the solvent in proton abstraction from the olefin has been discussed. The preparation[210] of (1-acetoxyalkyl-π-allyl)$PdCl/_2$ from substituted butadienes and $PdCl_2$ in HOAc/NaOAc has been reported.

Ring opening of methylenecyclobutane by $PdCl_2$ results in a mixture of the two π-allylic products (88), (89)[211]. The reaction of 1,1-dimethylcyclopropane with H_2PtCl_6 in Ac_2O, or in propionic anhydride however yields the cyclobutenium cations (90) and (91) respectively and $PtCl_6^{2-}$ [212].

2,2,4-trimethyl-3-pentenol reacts with $PdCl_2$ to give the π-allylic complexes,



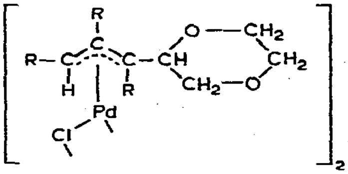
(88) (89)



R = Me (90)
R = Et (91)

{[$(CH_2CMeCH)\cdot CMe_2CH_2\cdot X$] $PdCl$}$_2$ where X = OAc for the reaction solvent $H_2O/HOAc$ and X = OH for dimethylformanide[213]. The platinum chloride reaction yields an olefin complex [$Me_2C{=}CHCMe_2CH_2O\text{-}PtCl$]$_2$ [213]. The dienols, $R_3R_4C{=}C(R_2)C(OH)(R_1)CH{=}CH_2$, with $PdCl_4^{2-}$ in MeOH give symmetric 1,5- or asymmetric 1,2-dimethoxy (π-allylPdCl)$_2$ derivatives depending on the structure of the dienol[214]. In diethylene glycol the reaction gave, by 1,2-addition, a dioxane derivative (92) or a polymeric product by 1,5-addition[214].

Allyl chloride and Na_2PdCl_4 in MeOH react with various reducing agents to give allylpalladium chloride. The yield depends on the nature of the reducing agent increasing in the order $Cu \sim Zn < Fe < TiCl_3 < CO < SnCl_2$[215]. The $SnCl_2$ preparation has also been used to prepare allylplatinum chloride in high yield[215]. The mechanism of the reaction of allyl chloride and higher homologs with $PdCl_2$ in presence of H_2O to give (π-allylPdCl)$_2$ species and diacetyl has been discussed[216].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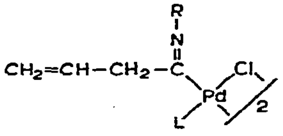

L = PhNC, PPh$_3$; R = Ph

(93)

Cleavage of allylsilanes by palladium halide salts in hydroxylic solvents has been found to give (π-allylPdCl)$_2$ and organic cleavage products such as $(Me_3Si)_2O$, Me_3SiOMe, and $CH_2{=}CHCH_3$ [217].

The interaction of $SnCl_2$ and (π-allyl)M$(PPh_3)_2$Cl gives the complexes [π-allylM$(PPh_3)_2$]-[$SnCl_3$] and [π-allylM$(PPh_3)SnCl_3$], where M = Pd, Pt[218].

(π-AllylPdCl)$_2$ reacts with RNC to produce (π-allylPd(RNC)Cl)[219]. This complex reacts with $SnCl_2$ and $GeCl_3^-$ to give [π-allylPd(RNC)M$'Cl_3$] and reacts with RNC or PPh_3 by rearranging to (93)[219]. Cyano-bridged tetramers such as [Pd(CN)π-allyl]$_4$ have been reported by Shaw *et al.*[220]. Studies of the modes of decomposition of (π-allylPdCl)$_2$ by Ph_4Pb[221] and by NaOMe/MeOH or NaOOCH/MeOH[222] have been reported.

Coordinatively unsaturated cations have been generated in THF solutions from allyl and enyl palladium and platinum species and reacted with ligands as shown[223]:

$$\mathrm{Pd}(\pi\text{-allyl})^+ \xrightarrow[\text{or } L_2\,=\,\text{Bipy, Diphos, COD}]{L\,=\,\text{phosphine, arsine}} [\mathrm{Pd}(\pi\text{-allyl})L_2]^+$$

$\mathrm{Pd(diene{-}OMe)^+} \rightarrow [\mathrm{Pd(diene{-}OMe)}L_2]^+$
diene = NBD, COD; L_2 = Bipy
diene = Dcp; L_2 = Bipy, COD

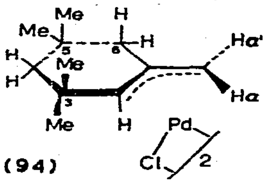
$\mathrm{Pt(Dcp{-}OMe)^+} \rightarrow [\mathrm{Pt(Dcp{-}OMe)}L_2]^+$
L = PPh_3
or L_2 = Bipy, COD, Dcp

On reaction with dry HCl, monomeric $Pt(all)_2$ gives a product $[ClPt(all)]_n$ whose structure depends on the nature of all. For all = allyl, $n = 4$ with both the allyl and the chloride bridging while for all = 2-methylallyl, $n = 2$ with bridging chlorides and π-2-methylallyl ligands[224]. The tetramer on reaction with Tl(Acac) gives a binuclear complex $[Pt(Acac)allyl]_2$. Reaction of $[ClPtall]_n$ with neutral ligands L gives products in which the allylic ligand is π-bonded. σ-Bonded allyls result in the reaction of EPh_3 (E = P, As) and $Pt(2\text{-methylallyl})_2$ to give $[Pt(\sigma\text{-2-methylallyl})_2(EPh_3)_2]$. The complexes $[ClPtall]_2$ could also be prepared by heating olefin complexes, $[PtCl_2(olefin)]_2$ with 50% aqueous HOAc[224].

As part of a larger study on the reactivity of transition metal sandwich cations and β-diketonates, the acetyl-acetonato, dibenzoylmethanato, and ferrocenoyltrifluoroacetonato complexes of allylpalladium were prepared and their electronic spectra recorded[225].

In a general paper on optical activity in asymmetric transition metal complexes, allylic palladium derivatives have been cited as examples of optically active complexes which have asymmetric centres in the ligands[226].

The dynamic stereochemistry of π-allylic palladium complexes is an area of continued investigation. The mechanism for syn—anti allylic proton exchange has been confirmed to be a $\pi \rightarrow \sigma \rightarrow \pi$ process in which the intermediate contains a σ-allylic unit. The complex (94) has been found to be particularly useful for such studies since it gives several alternative site exchanges for the measurement of the parameters of the exchange[227]. Several groups of researchers have proposed and supported the $\pi \rightarrow \sigma \rightarrow \pi$ mechanism from studies of the asymmetric allyl systems, (π-allyl)Pd(L)X. The Shell research laboratories have published investigations of the dynamic stereochemistry of these substituted allyl complexes where X = Cl, OOCR; L = PMe_2Ph[228]. Exchange of the R′, R″ groups in substituents at the 2-position of the allyl complex (95) has been observed only when *syn—anti* (3,4) exchange is observed. The authors argue on the basis of this observation that a flip mechanism wherein the metal flips from one face of the allyl to the other does not operate. If the 2-substituent is a bulky isopentyl or isobutyl group (3,4) exchange is inhibited in (95) and (1, 2, 3, 4) exchange is the first observed process on raising the temperature. The authors attribute this inhibition to the sterically hindered rotation of the 2-substituent required during the (3, 4) exchange[228].



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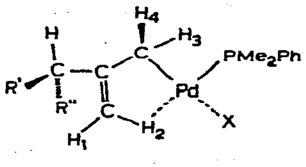
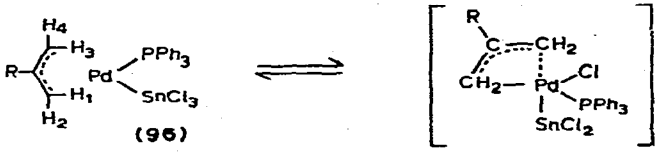


(95)

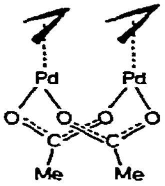
For systems such as [(1-acetyl-2-methylallyl)PdCl(amine)] assignment of peaks has been achieved for the *syn* and *anti* isomers in $CDCl_3/C_6H_6$ solution by comparison with model compounds and by nuclear Overhauser techniques[230]. The (disubstituted-π-allyl)-PdCl(amine) systems have been studied by a variety of NMR techniques to determine steric factors and kinetic parameters. Use of spin saturation experiments has enabled Faller *et al.* to distinguish the processes occurring in the observed collapse of the *syn* and *anti* protons of the two isomers of (1-acetyl-2-methylallyl)PdCl(Py) in solution[230].

Variable temperature NMR studies on π-allyl and π-2-methylallylPdPPh$_3$(SnCl$_3$) (**96**) have been interpreted in terms of an intermediate (**97**) during H^2–H^4 and H^1–H^3 proton site interchange[231].



(97)

The presence of two conformers of π-allylPd-carboxylate dimers has been shown by variable temperature NMR studies[224]. An intramolecular process has been noted at low temperatures which exchanges the environments of the allyls in the isomer (**98**). At higher temperatures equivalence of all the allylic units via a bimolecular exchange occurs. Allyl ligand exchange in the system (π-all)PdCl/$_2$ and (π-all)Pd(OAc)/$_2$ has been ascribed to the intermediacy of a mixed species[229]. The related triazene systems, (π-allyl)Pd(PhNNNPh)/$_2$ and (π-allyl)Pd(PhNNNMe)/$_2$, also have several conformers in solution but the NMR spectra are temperature invariant[232]. Trofimenko has reported the preparation of the dimeric pyrazole complexes (π-allylic)Pd(pyrazole)/$_2$ and (**99**)[233]. These π-allylic complexes were stereochemically non-rigid[233].



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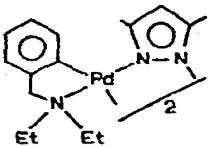
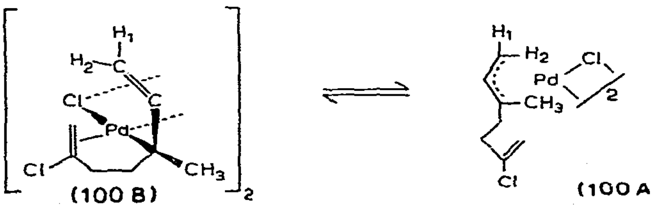
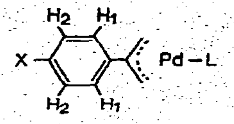


(99)

The presence of a terminal vinyl group in complex (**100A**) (obtained from the insertion of isoprene into (2-chloroallyl)PdCl/$_2$) leads to preferential isomerization of the *syn*- and *anti*-isomers in solution before the exchange of *syn/anti* protons H^1 and H^2 occurs[234]. The isomerization takes place via a σ-allylic intermediate (**100B**) stabilized by chelation involving the terminal vinyl group.



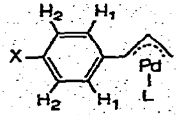
The difference in the chemical shifts ($\Delta\partial$) of the H^1 and H^2 protons of both (**101A**) and (**101B**) has been found to be dependent on X and L[235]. A fairly good linear plot of $\Delta\partial$ against σ_p^+ of X gave intercept values (for $\Delta\partial = 0$) of $\sigma_p^+ = 0.27$ (a); 0.24 (b); 0.21 (c)



(101 A)

L = Acac, (c)
L = Cp, (d)

X = Br, Cl, H, CH_3, CH_3O



(101 B)

L = Acac, (a)
L = Cp, (b)

and 0.03 (d) corresponding to the σ_p^+ substituent constants of the 1-(a and b) and 2-(c and d) positions in the π-allylpalladium-L complex[235].

A survey of the influence of ligands on the activity and specificity of transition metal catalysts includes a discussion of the oligomerization of butadiene via allyl-nickel species[236].

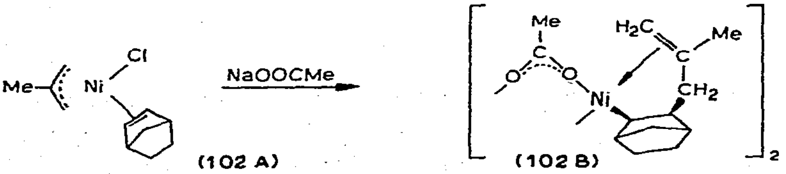
Addition of PRF_2 to allylmetal halides results in ligand coupling[237].

$$(\pi\text{-2-R}'\text{-allyl})MX/_2 + 8RPF_2 \rightarrow 2CH_2 = CR'{-}CH_2X + 2M(PRF_2)_4 \ (M = Ni, Pd).$$

(π-allylNiOOCCF$_3$)$_2$ dimerizes styrene stereospecifically to *trans*-1,3-diphenyl-1-butene[238]. Aromatic substitution has not been found to influence the reaction whereas olefin substitution inhibits it completely.

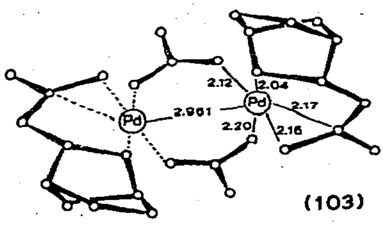
Norbornene insertion into the allyl–palladium bond occurs at the least-substituted terminal allylic carbon of the complexes (π-all)Pd(hfacac) to give enyl complexes which are structurally analogous to (**102B**)[239]. The nickel complex (**102A**) is obtained by addition of norbornene to [(π-2-methylallyl)NiCl]$_2$ [240]. Reaction of (**102A**) with NaOAc gave (**102B**).

An X-ray structural study of the palladium analog (**103**) has verified *exo-cis* insertion of the norbornene as postulated for the two previous systems[241].



(102 A)

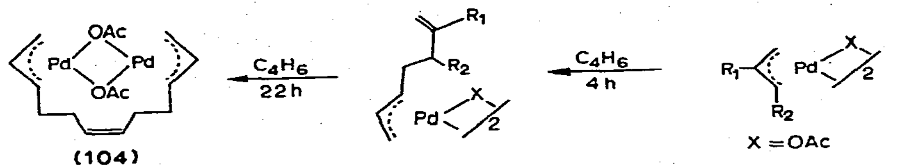
(102 B)



(103)

Addition of 1,2- or 1,3-dienes to π-allylic PdX (X = Cl, Acac, or hfacac, Pd/diene $\geqslant$ 1) gives *syn/anti* exchange via a $\pi \rightarrow \sigma \rightarrow \pi$ process involving reversible coordination of the diene to give a σ-allylic (π-olefinic) species before the formation of insertion products[242]. The rate of product formation therefore is not dependent on coordination of diene to give the σ-intermediate. The rate of product formation (for butadiene) correlates with the relative stability and hence the lifetime of the σ-species. The conclusion reached is that the rate-determining step is the actual diene insertion[242]. Medema and Van Helden[243] have also reported the nature of the reactions of conjugated and cumulative dienes with π-allylic palladium halides. For conjugated dienes, substitution occurs at the most substituted allylic carbon (contrary to the mode of substitution for CO and allene) with the rate decreasing for X = Cl > Br > I and for α- and β-allyl substituent Cl > COOR ≫ H > Me.

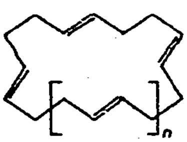
(π-Allyl)PdOAc/2 has been used as a catalyst for a variety of butadiene reactions[244]. In C_6H_6, n-dodecatriene is produced via the isolable complex (**104**). In the presence of PPh$_3$, linear dimers are obtained. In MeOH, the butadiene is converted to octadienyl, dodecatrienyl or hexadecatetraenyl methyl esters depending on the reaction conditions[244]. Dodecatetraene has been reported as the product of the catalytic reaction of butadiene with a series of allylPd chelates[245]. ^{1}H NMR studies on the system butadiene + (π-allyl-PdX)$_2$ (X = halide) have been reported[246,247]. In the latter study, small amounts of diene have led to a *syn/anti* proton exchange (observable in the NMR) which depends on the concentration of $[\text{dimeric complex}]^{1}$ and $[\text{butadiene}]^{0.5}$ and which correlates with the rate of polymerization with different allyls and X. It has also been noted that the electrical conductivity of the system increases exponentially over this concentration range suggesting that ions are present[247]. NMR studies of the reaction of (π-crotylNiI)$_2$ with butadiene have been reported for three cases involving: C_4D_6, perdeuterated complex and undeuterated reagents[248].



(104)

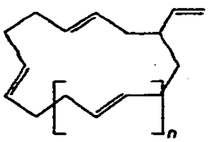
X = OAc

Insertion of the 1,3-diene occurs at the least substituted terminal allylic carbon in contrast to the above palladium systems[248,249]. The interaction of butadiene with the catalyst system (π-allyl)$_2$Ni and [(π-allyl)NiCl]$_2$ results in a mixture of cyclic dimers, trimers, a high boiling fraction containing cyclopolyenes of the types (**105A**), (**105B**) and a waxy residue[250].



(105 A)

$n = 1-6$



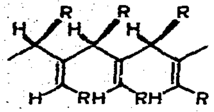
(105 B)

$n = 1-6$

In the presence of an organic peroxide (such as benzoyl peroxide) [π-allylNiX]$_2$ polymerizes butadiene (and vinyl ether) stereospecifically to 90% *cis*-1,4 content polymer. The active catalyst is thought to be a benzene insoluble nickel complex which is composed of oxygen, halogen, a σ-allyl, and nickel[251,252].

Polymers of 1,3-disubstituted propadienes give interesting possibilities since the basic unit of the polymer has an asymmetric center and trisubstituted double bond present[253]. Polymers generated by (π-allyl)NiI/$_2$ from optically active monomer contain sequences of stereoregular structure and are optically active which requires structure **(106)**.

$(PPh_3)_2Ni^0$ catalytically converts allene into a mixture of oligomers[254]. The initially formed complex, $(Ph_3P)_2NiC_3H_4$, was isolated and characterized. Mechanistic routes have been discussed in light of the reaction products and the products from competitive experiments with ethylene and methyl acrylate[254]. With $Ni(COD)_2$ as catalyst 1,2,4,6,9-pentamethylenecyclodecane is the sole product[255]. An unstable complex which has been isolated from the reaction and formulated as $Ni(C_9H_{12})$ has been treated with PPh_3 to give **(107)**[255].



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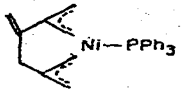

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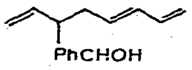

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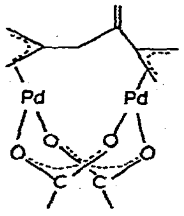

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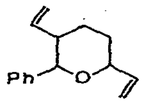


(110)

(108) has been obtained by direct reaction of allene and $Pd(OAc)_2$ or by insertion of allene into (2,2-bi-π-allyl)$Pd_2(OAc)_2$[256].

(π-allyl)PdCl/$_2$ + NaOPh + PPh_3 provide a catalytic system for the reaction of butadiene with PhCHO to produce **(109)** and **(110)** in a ratio controlled by the ratio of Ph_3P to Pd. An explanation of this control is offered[257].

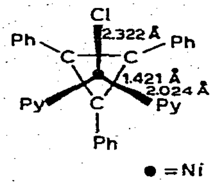
IX. DELOCALIZED CARBOCYCLIC COMPLEXES

Two π-cyclopropenyl nickel complexes have had their full molecular structure published; $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3Ph_3)$[258] (see preliminary structure AS 1970, p. 252) and its analog $(\pi\text{-}C_3Ph_3)NiCl(Py)_2 \cdot Py$ **(111)**[269]. The nickel-ring distance in **(111)** is 1.941 Å (as compared to 1.961 Å for $(\pi\text{-}C_3Ph_3)Ni(\pi\text{-}C_5H_5)$)[259].

Combination of the appropriate dichlorocyclobutene compounds with $Ni(CO)_4$ gives the partially and tetra-alkylated cyclobutadiene complex **(112)**[260].

Attempts to liberate cyclobutadiene from nickel or palladium complexes by the addition of dithiolene have led instead to $(\pi\text{-}C_4Me_4)NiS_2C_2(CN)_2$ and $(\pi\text{-}C_4Ph_4)PdS_2C_2(CN)_2$[261].

The acetylenes RC≡CR (R = Ph, p-ClC_6H_4, p-MeC_6H_4, p-$MeOC_6H_4$) combined with $(PhCN)_2PdCl_2$ in C_6H_6 or EtOH (except for the last case) to give on treatment with HX the complex $[(\pi\text{-}C_4R_4)PdX_2]_2$. The complexes will undergo ligand-transfer reactions as shown in Scheme 6[262].



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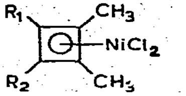
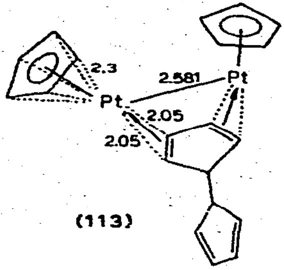


(112)

$R_1 = R_2 = H$
$R_1 = CH_3, R_2 = H$
$R_1 = CH_3, R_2 = Et$
$R_1 = R_2 = Et$
$R_1 = CH_3, R_2 = i\text{-}Pr$
$R_1 = R_2 = i\text{-}Pr$

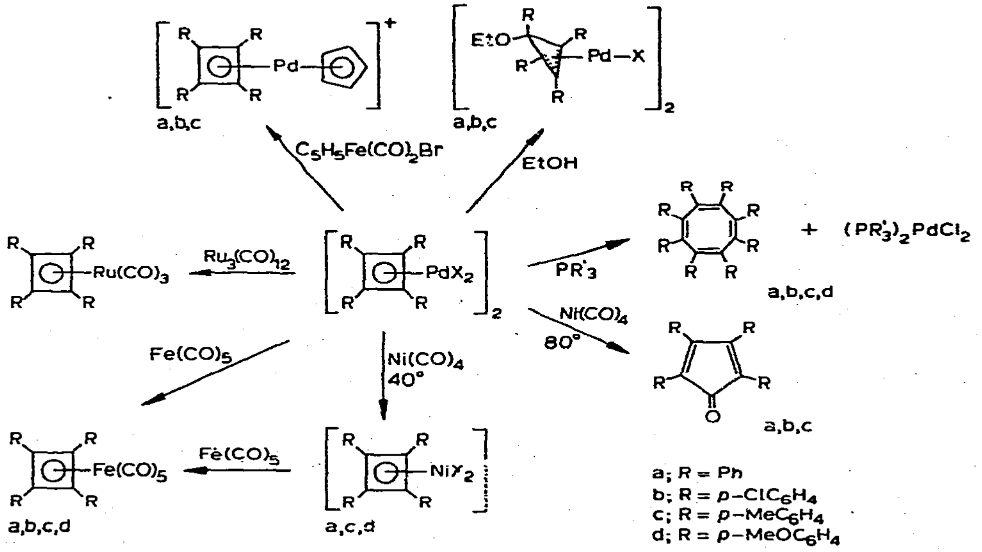


(113)

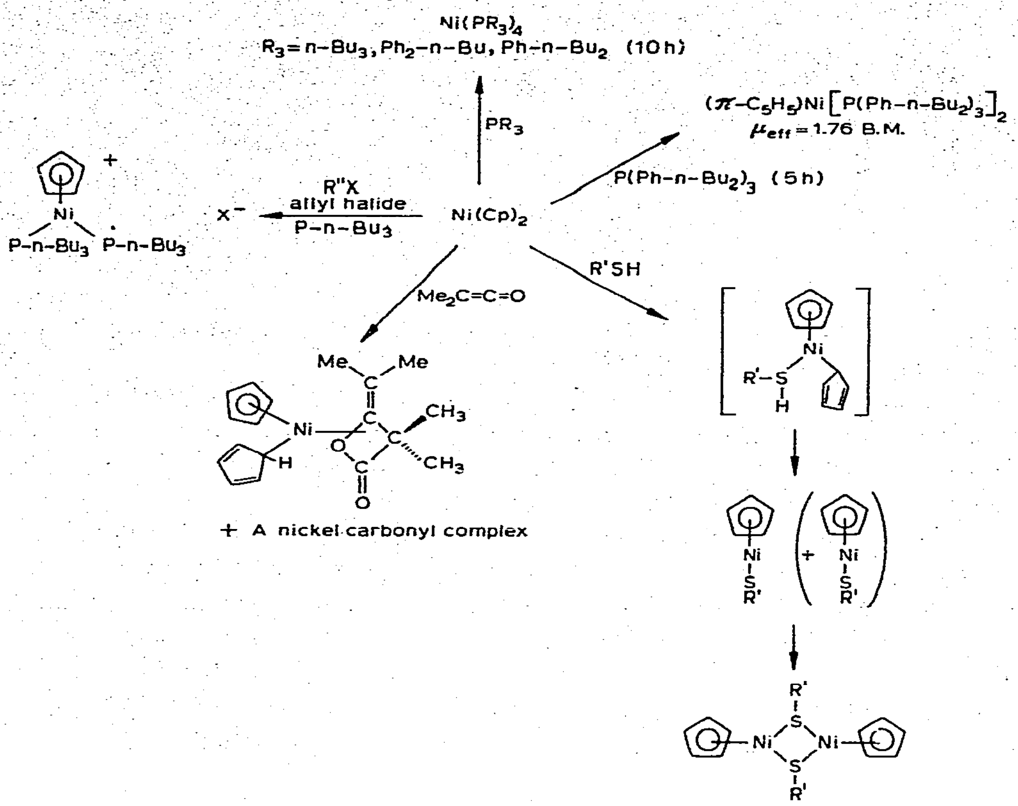
Reaction of $Pt(CO)_2Cl_2$ + PhC ≡ CPh in ether gives tetracyclone, hexaphenylbenzene and the Pt complex, $[(\pi\text{-}C_4Ph_4)PtCl_2]_n$[263].

The product of the reaction of $Na(C_5H_5)$ and $PtCl_2$ has the unusual structure (113)[264]. Raman spectra of $(\pi\text{-}C_5H_5)PtMe_3$ have been recorded in solid and solution states with assignment of the polarized lines at 561, 263 cm^{-1} to symmetric Pt–Me and Pt–(ring) stretching vibrations consistent with a *pentahapto* C_5H_5 ring[265].

$Ni(\pi\text{-}C_5H_5)_2$ has been investigated by several physical techniques. X-ray PES recorded the molecular core binding energies of transition metal carbonyl and cyclopentadienyl complexes including $Ni(CO)_4$ and $Ni(\pi\text{-}C_5H_5)_2$[266]. Polarographic behaviour of nickelocene showed reversible oxidation to $(C_5H_5)_2Ni^+$ and $(C_5H_5)_2Ni^{2+}$ and irreversible reduction to $(\pi\text{-}C_5H_5)(\pi\text{-cyclopentenyl})Ni$[267]. Under polarographic conditions $(\pi\text{-}C_5H_5)(Ph_3P)NiCl$ disproportionates to give nickelocene[267]. On the basis of ^1H NMR contact shifts for three nickelocenium cations, the presence of a π-delocalization has been established[268].



Scheme 6. Reactions of $[(\pi\text{-}C_4R_4)PdX_2]_2$.



Scheme 7. Preparations from nickelocene.

A preparation of substituted nickelocenes from Na/THF and EtC_5H_5 in the presence of $Ni(NH_3)_6Cl_2$ has been reported[269]. The catalysis by nickelocene of the decomposition of $(\pi\text{-}C_5H_5)Ni(CO)_2$ in DMSO has been investigated[270].

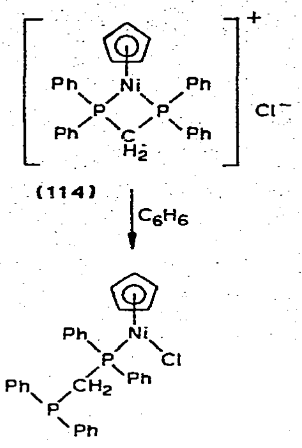
Reactions using nickelocene as a reagent are shown in Scheme 7[271,272,273,274]

Germyl derivatives of $(\pi\text{-}C_5H_5)Ni$ complexes have been generated by two methods one of which uses nickelocene[275].

The ionic chloride in $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ may be replaced by $X^- = NCO^-, NCS^-, N_3^-, ClO_4^-, ClO_3^-, NO_3^-$ and NO_2^-. Except when $X = ClO_4$ or NO_3, the original chloride and the products dissociate in non-polar solvents or above their melting points[276,277].

$$[(\pi\text{-}C_5H_5)Ni(PBu_3)_2]^+\,X^- \xrightleftharpoons[+\,PBu_3]{\Delta,\ \text{solvent}} \pi\text{-}C_5H_5NiX\cdot PBu_3 + PBu_3$$

Treatment of the chloride salt with $Ph_2P(CH_2)_nPPh_2$, ($n = 1$), gave (**114**) which in benzene gave (**115**)[278]. The other chelating phosphines gave similar chelating cations for



(114)

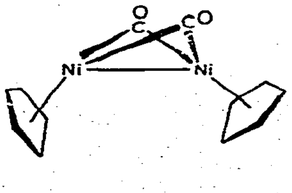
(115)

$n = 2$ to 4[278]. Reaction of $Tl(C_5H_5)$ with $(R_3P)_2Pd_2X_4$ (R = Et, i-Pr, Ph; X = Cl, Br, I) or $(R_3P)_2MX_2$ gives the analogous covalent complexes $(R_3P)(\pi\text{-}C_5H_5)PdX$[279]. The complexes $(\pi\text{-}C_5H_5)(R^1{}_3P)PtR^2$ (R^2 = Ph, *o*-tolyl for R^1 = Et and $R^2 = C(O)Ph$ for R^1 = n-Bu) were obtained from $[(R^1{}_3P)R^2PtX]_2$. The covalent compounds so formed react with phosphines to give salts (as above) or unstable σ-bonded C_5H_5 complexes depending on the solvent and phosphine used[279].

The dimer, $[(\pi\text{-}C_5H_5)NiCO]_2$, has been assigned a solvent independent puckered bridge stereochemistry (**116**)[280]. Two studies on the kinetics of reactions of this dimer followed by infrared spectroscopy have been published[281,282].

$$[(\pi\text{-}C_5H_5)NiCO]_2 + 2L \rightarrow Ni(CO)_2L_2 + Ni(\pi\text{-}C_5H_5)_2$$

For L = $AsPh_3$, $P(OPh)_3$, PPh_3 and $PEtPh_2$ in toluene, decalin and THF, a second order rate law was followed, first order in each reactant[281]. Another study on this reaction, in petroleum ether or n-heptane noted the reaction as being S_N2 for L = CO, $PClPh_2$, PPh_3 and P-n-Bu_3[282]. For L = PhC≡CPh the products for this reaction have been described as $(\pi\text{-}C_5H_5)_2Ni_2(PhC{\equiv}CPh) + 2CO$. A two-stage mechanism with a reversible, first order process as the rate-determining step has been proposed[282]. The thermal insertion of SnX_2



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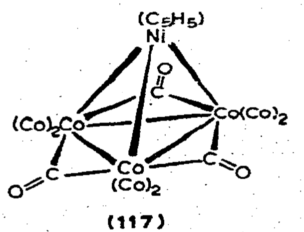

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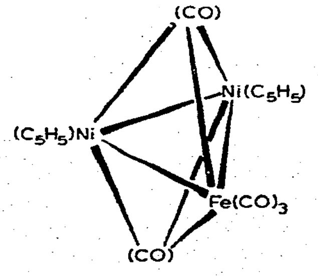


(118)

(X = Cl, Br) into the nickel–nickel bond of the dimer was followed spectrophotometrically at 600 nm. The resulting kinetic data have been interpreted in terms of a bimolecular mechanism involving direct attack of the tin halide on the dimer[283]. Reaction of $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ with other metal carbonyl species has resulted in the preparation of $(\pi\text{-}C_5H_5)NiCo_3(CO)_9$, $(\pi\text{-}C_5H_5)_2Ni_2Fe(CO)_5$ and $[Me_4N][(\pi\text{-}C_5H_5)_2Ni_2Mn(CO)_5]$ which have all been characterized[284]. On the basis of IR studies structure (**117**) has been suggested for the cobalt compound; and structure (**118**) for the iron complex in the solid state and for the manganese anionic complex. In solution a mixture of isomers appears probable for the last two compounds. Reactions of the dimer with $Ru_3(CO)_{12}$ and $Mo(CO)_5\cdot THF$ gave the known compounds $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ and $[\pi\text{-}C_5H_5Mo(CO)_3]_2$[284].

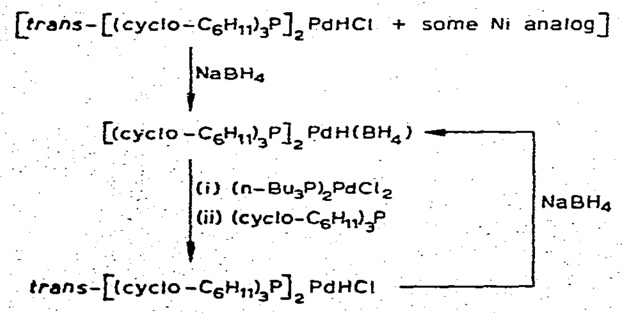
X. HYDRIDO COMPLEXES

The nickel hydride complexes, *trans*-$(PR_3)_2NiHX$ (X = halogen, SCN, CN; R = C_6H_{11} or i-Pr), have been prepared by the reaction of *trans*-$(R_3P)_2NiX_2$ and $NaBH_4$[285]. Preparation of the palladium complexes by this route failed. The stable palladium complexes *trans*-$(R^1{}_3P)_2PdHX$ (X = Cl, Br, I, NCS) were produced instead using the nickel borohydride, *trans*-$(R_3P)_2NiH(BH_4)$, as the reducing agent. The nature of this reaction was followed by NMR and found to involve a reduction and subsequent phosphine exchange between the hydride complexes to give a mixture of six hydride phosphine complexes. Subsequent reaction via the cyclic Scheme 8, allowed complete removal of the nickel analog in two cycles and increased the amount of $(R^1{}_3P)_2PdHX$ present[286].

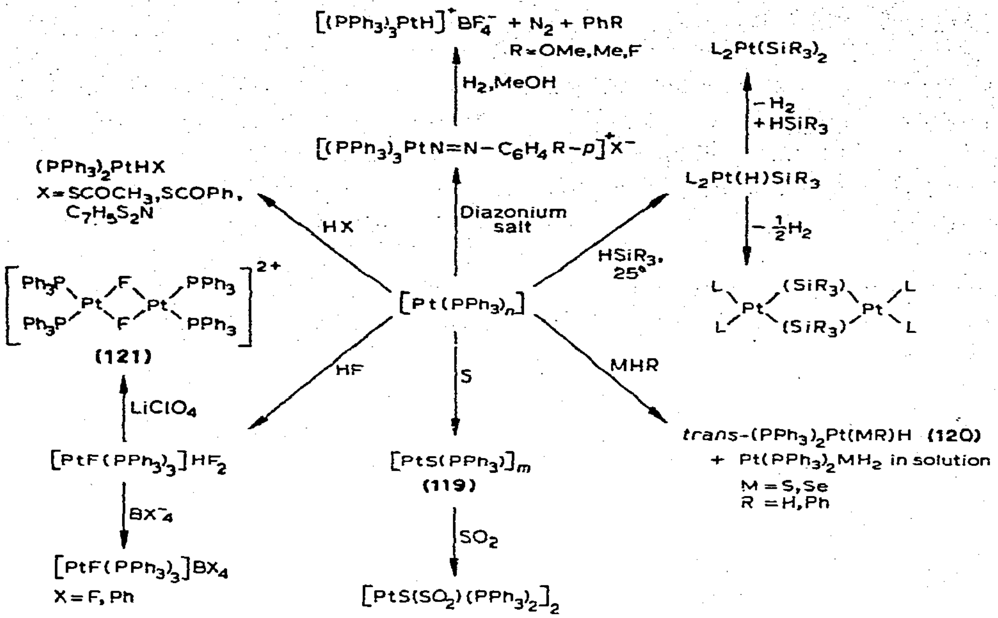
Birnbaum has noted the hydride chemical shift increases $X = I < Br < Cl$ in *trans*-$[(PEt_3)_2MHX]$ (M = Pd, Pt) and in *trans*-$[(AsMe_3)_2PtHX]$ with $Pd < Pt$[287].

A correlation of decreasing metal–hydride stretch with increasing *trans*-activity for the *trans* ligand L has been documented in the infrared study of a series of platinum(II) hydrides[288,289].

Oxidative addition of HX to $Pt(PPh_3)_2$ in the presence of excess HCl has previously been described as affording a Pt^{IV} species, $(PPh_3)_2PtH_2Cl_2$. On the basis of spectral data on the complex in solution and solid, Dumber and Roundhill conclude the "Pt^{IV} dihy-



Scheme 8. Purification of crude product in the preparation of *trans*-$[(cyclo\text{-}C_6H_{11})_3P]_2PdHCl$.



Scheme 9. Preparations from $Pt(PPh_3)_n$.

dride" phase, is actually *trans*-$(PPh_3)_2PtHCl$ in a different crystalline state[290]. Oxidative addition to $Pt(PPh_3)_n$ provides a synthetic route to Pt-hydrides, Scheme 9[291,292,293,294,295]. The behaviour of adducts (**120**) and (**119**) towards oxygen, $HC{\equiv}CH$, $H_2C{=}CH_2$ and $C{\equiv}O$ has been related to poisioning in platinum metal catalysis[295]. The reaction of HF with $Pd(PPh_3)_4$ gives a dimeric dication, $[PdF(PPh_3)_2]_2F_2$, analogous to (**121**), and with $PtY_2(PPh_3)_2$ (Y = Cl, Br) gives *cis*-$PtYF(PPh_3)_2$[291].

The oxidative addition of $HSnMe_3$ to the chelated complexes (Diphos)$PtCl(SnMe_3)$ or (Diphos)$Pt(SnMe_3)_2$ yields the octahedral complexes (Diphos)$Pt(H)Cl(SnMe_3)_2$ and (Diphos)$Pt(H)(SnMe_3)_3$[296]. Hydrogenolysis of (Diphos)$Pt(SiMe_3)_2$ causes the loss of trimethylsilane to give at 25° the hydride [(Diphos)$Pt(SiMe_3)H$] while at higher temperatures a $(Diphos)_3Pt_4$ cluster compound is formed[296].

Halogen exchange in the reaction of *trans*-$(PEt_3)_2PtHX$ with $MH_{4-n}X_n$ (M = Si, Ge; X = Cl, Br, I; n = 0–3) in C_6H_6 leads to *trans*-$(PEt_3)_2PtX(MH_{3-n}X_n)$ in which the heavier halogen is bound to the metal for the MH_3Y case (Y = F, Cl, Br, I)[297]. Addition of MH_3X to the diiodide *trans*-$(PEt_3)_2PtI_2$ gives a six coordinate complex, $(PEt_3)_2Pt(MH_2X)(H)I_2$ which loses H_2 at room temperature to give *trans*-$(PEt_3)_2Pt(I)(MHXI)$[297].

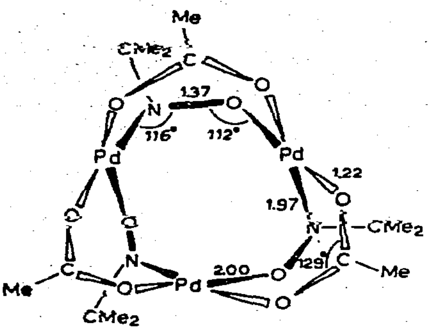
CS_2 insertion for *trans*-$(PR_3)_2PtHX$ (R = Ph, Et; X = Cl, Br, I, CN) gives an *S*-bonded derivative $PtX(S_2CH)(PR_3)_2$ in what has been described on the basis of a kinetic study as a two step process involving a second-order coordination of complex and CS_2 followed by an intramolecular rearrangement[298].

XI. MISCELLANEOUS COMPLEXES

Mawby and Pringle have published the full structure of $[Pd(OAc)(ONCMe_2)]_3 \cdot 1/2C_6H_6$ (122) obtained by displacement of acetate from $[Pd(OAc)_2]$[299]. The square planes of the metals tilt inwards to reduce the span bridged by the acetoximate groups.

The rapid, thermally reversible, addition of conjugated dienes to [cis-(1,2-perfluoromethylethene-1,2-dithiolato)]nickel gives adducts of the type (123) with 1,3-dimethylbutadiene[300].

A tertiary phase equilibria study in the system U–Pt–C has shown the existence of the ternary carbide U_2PtC_2 which is formed peritectically in equilibrium with UC, U_2C_3, UPt_3, UPt_2 and C[301].



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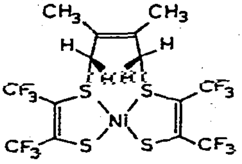
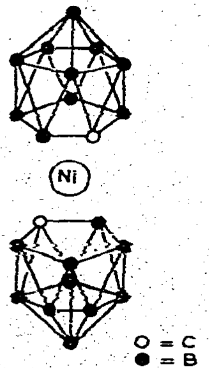


(123)

Two papers have appeared dealing with the reductive alkylation and ring opening of a nickel corrin system[302] and the alkylation and rearrangement of a nickel corrole[303].

$Cs(B_3H_8)$ reacts with L_2PtCl_2 in acetonitrile/NEt_3 to give complexes $L_2PtB_3H_7$ (L = PEt_3, PPh_3, $PEtPh_2$, $P(o\text{-tolyl})_3$)[304]. The platinum has been assigned an oxidation state of +2 on the basis of the Pt 4f7/2 molecular core binding energies. A π-borallyl structure analogous to π-allyl has been suggested[304]. 2,2'-Dilithiobiscarborane reacts with $NiBr_2$ in anhydrous Et_2O to give the diamagnetic anion, $(Et_4N)_2Ni[(B_{10}C_2H_{10})_2]_2$ which has



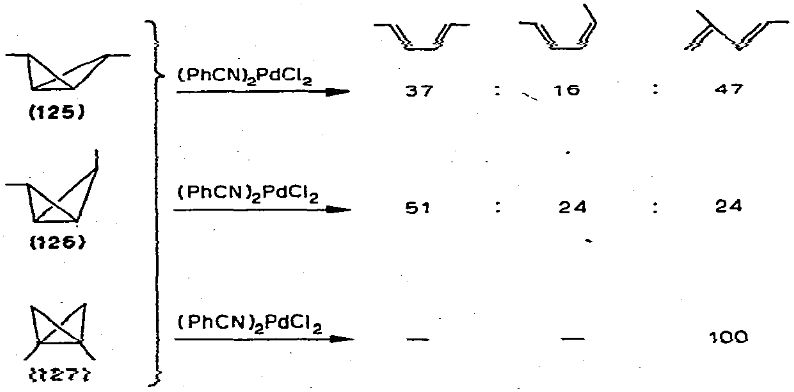
(124)

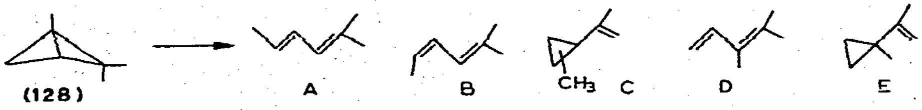
been characterized as a square planar structure (see AS 70, p. 256)[305]. Treatment of the carboranes $B_{10}H_{12}CH^-$ and $B_{10}H_{12}NH_3$ with strong base (Li-n-Bu or NaOH) in the presence of $NiCl_2$ has given the metallocarboranes $(B_{10}H_{10}CH)_2Ni^{2-}$ and $(B_{10}H_{10}CNH_3)_2Ni$ in which a formal oxidation state of IV has been stabilized by the ligands[306]. *N*-Alkylated carborane, $B_{10}H_{12}CNH_2CH_2Ph$, gives $[(B_{10}H_{10}CNH_2CH_2Ph)_2Ni]$ and methylation of $(B_{10}H_{10}CNH_3)_2Ni$ with dimethylsulfate will give the dimethylated metallocarborane. Treatment of $(B_{10}H_{10}CNH_3)_2Ni$ with nitrous acid gives $(B_{10}H_{10}COH)_2Ni^{2-}$ which illustrates the stability of the basic unit (124)[306].

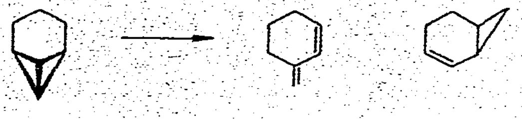
XII. REARRANGEMENT OF STRAINED POLYCYCLIC HYDROCARBONS

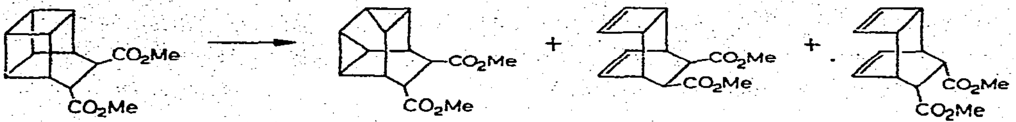
Considerable interest has developed in the use of metal catalysts to overcome the principle of conservation of orbital symmetry in concerted organic reactions.

An extensive survey has been carried out on the influence of various transition metal species on an electrocyclic ring opening of hexamethyl-Dewar-benzene to yield hexamethylbenzene. No apparent correlation between activity and the metal *d* configuration (d^8–d^{10}) was noted[307]. Among the active catalysts (with conversion %) were $(PhCN)_2NiCl_2$ (8%), $(PhCN)_2PdCl_2$ (21%), $PdCl_2$/EtOH (100%), $PdBr_2$/EtOH (100%), $[Pd(C_2H_4)Cl_2]_2$ (60%), and 10% Pd on C (5%)[307]. A comparison of Ag^I and Pd^{II} isomerization of bicyclobutane reveals that the metals were different in product distribution and substituent effects. The product distribution for (125), (126) and (127) for $(PhCN)_2PdCl_2$ catalyst shows the sensitivity of the reaction course to substituents[308]. The mode of cleavage of (128) has also been shown to be dependent on the ligands in the catalyst[309]. $(PhCN)_2PdCl_2$ gave 13/1 = D/E; π-allyl $PdCl/_2$ gave 3% of C and 72% of 3/46/41 = D/A/B and (1-chloromethyl-π-allyl)$PdCl/_2$ gave 3% of C and 40% of 55/26/19 = D/A/B. At low






(129) (130) (131)



(132) (133) (134) (135)

catalyst concentrations ligand exchange involving the diene D was observed and in all cases the catalysts slowly promoted polymerization of the products[309]. (129) was catalytically ring opened to (130) by [π-allylPdCl]$_2$ and $(PhCN)_2PdCl_2$[308,311] and to (130) 62% and (131) 24% by PtO_2[310,311]. Mechanistic considerations for these processes have been discussed[308,311]. Another transition metal catalyzed isomerization involves the 1,1^1-bishomocubane system (132) which opens to give (133)–(135) in the presence of Ag^I, Pd^{II}, Rh^I catalysts[312].

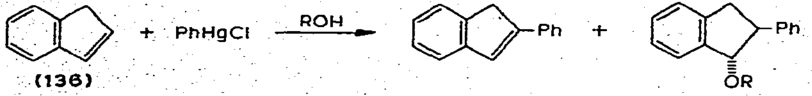
XIII. REACTIONS WITH OTHER ORGANOMETALLIC COMPOUNDS

Reactions of nickel and palladium compounds with organometallic compounds of other metals has led to a variety of coupling and exchange reactions. Pd^{II} salts in the presence of nucleophiles X = OAc, N_3, Cl, NO_2, Br, CN, SCN couple the aromatic substituents of HgR^+ according to[313]:

$$2RHg^+ + Pd^{II} + X^- \rightarrow R_2 + Pd^0 + 2Hg^{2+} + X^-$$

Addition of oxidants (Cr^{VI}, $Pb(OAc)_4$, etc.) changes the course of the reaction to give RX, Hg^{2+} and Pd^{II} as products[313]. Similar coupling reactions occur for 2RXC=CRHgX and R_2C=CHHgX in the presence of Pd^{II} to give RXC=CR–CR=CXR and R_2C=CH–CH=CR_2[314].

The aromatic substitution of olefins by RHgCl in the presence of Pd^{II} has been carried out for two cases. PhHgCl reacts in protic solvents in the presence of $PdCl_4^{2-}$ to give two types of addition products for (136) and (137) whose ratio depends on the solvent system[315]. The α,β-unsaturated acyl chlorides (*e.g.* CH_2=CHCOCl) give, on reaction with PhHgX



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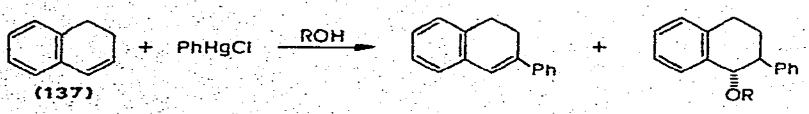
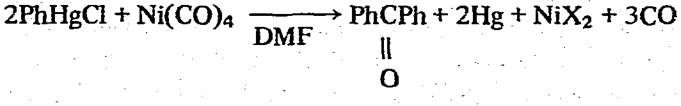


(137)

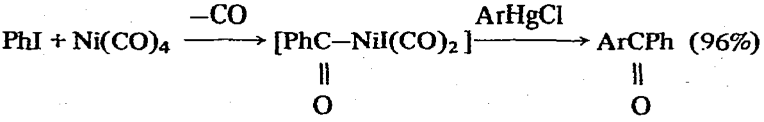
(Pd^{II} catalyst), ketene derivatives (10.5%) (isolated as saturated esters on reaction with alcohols) along with unsaturated esters (1.8%)[316].

Diaryl or dialkyl ketones have been prepared in excellent yield (95%) from the reaction[317].



$$2PhHgCl + Ni(CO)_4 \xrightarrow[DMF]{} Ph\underset{\underset{O}{\|}}{C}Ph + 2Hg + NiX_2 + 3CO$$

This reaction has been adapted to produce unsymmetrical ketones[317].



$$PhI + Ni(CO)_4 \xrightarrow{-CO} [Ph\underset{\underset{O}{\|}}{C}-NiI(CO)_2] \xrightarrow{ArHgCl} Ar\underset{\underset{O}{\|}}{C}Ph \quad (96\%)$$

Biaryls can also be obtained from the thallium complexes, $PhTlX_2$ ($X_2 = (OAc)_2, Cl_2, (O_2C_2F_3)_2, ClO_4(OAc)$, and PhCl) in a reaction with $PdCl_2/NaOAc$ to give yields of Ph—Ph up to 59%[318].

$Pd(OAc)_2$ catalyzes the reaction of ferrocene and olefin ($CH_2{=}CHX$, X = Ph, CN, CO_2Me, CHO, n-BuO) to produce alkenylferrocenes with the rate of reaction increasing with the electronegativity of the olefin substituents[319].

Alkyl Grignard reagents undergo a variety of reactions with nickel and palladium compounds. Substitution at a phosphine phosphorus in $(PPh_3)_2NiCl_2$ by MeMgBr followed by hydrolysis gives a mixture of products, PhH, PhMe, Ph_2, Ph_2MeP and $PhMe_2P$ although reaction between free PPh_3 and MeMgBr does not occur[320]. The structures of Grignard compounds produced by alkyl—olefin exchange:

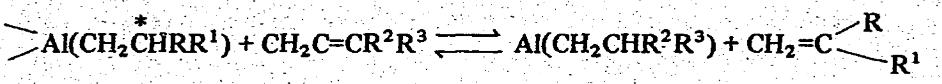
$$RCH{=}CH_2 + C_2H_5MgX \xrightarrow{NiCl_2} CH_2{=}CH_2 + RCH_2CH_2MgX + CH_3CH(R)MgX$$

or olefin insertion

$$RCH{=}CH_2 + PhMgX \xrightarrow{NiCl_2} PhC(R)HCH_2MgX + PhCH_2CH(R)MgX$$

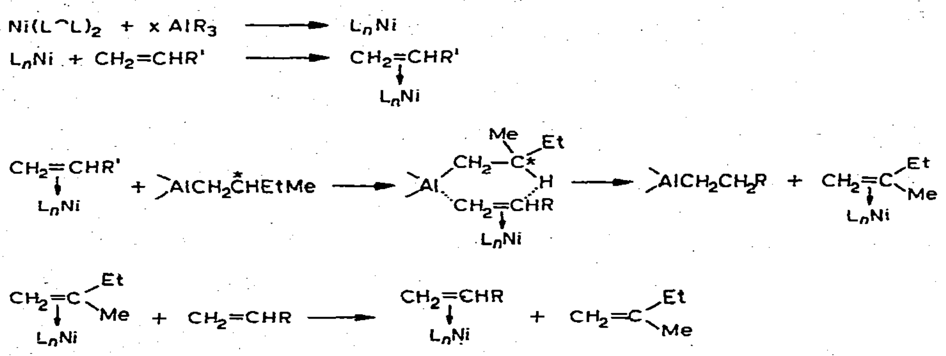
have been analyzed for a variety of olefins and Grignards[321]. Reactions of alkyl Grignards with NiX_2 or PdX_2 (X = halide) have been postulated to occur via an alkyl transition metal species which decomposes to dialkyl or to an alkene and an alkane (disproportionation). Oxidative coupling was favoured by Ag^I or Cu^{II} catalysts and by alkyl groups without a β-hydrogen[222]. Disproportionation is the common route for other cases.

Exchange reactions have been observed in the interaction of α-olefin and optically active compounds of Be, Zn, B and Al in the presence of Ni^{II} compounds containing chelating ligands[323].



$$>Al(CH_2\overset{*}{C}HRR^1) + CH_2C{=}CR^2R^3 \rightleftharpoons Al(CH_2CHR^2R^3) + CH_2{=}C\begin{matrix}R\\R^1\end{matrix}$$

By the variation in stereoselectivity and the difference in catalytic activity, it has been concluded that at least one chelating ligand is retained in the active catalytic species. Alkylation and subsequent hydride formation appear to play an unimportant role in the catalytic process on the grounds that for bis(*N*-alkylsalicylaldimino)$_2$ nickel there is a lack of activity in the racemization of optically active 2-methylbutylberyllium and aluminum derivatives[323]. The mechanism shown in Scheme 10 is proposed. The kinetics of this reaction has been found to be complex including an induction period and a first order dependence on nickel, olefin, and aluminum linked 2-methylbutyl groups[324].



Scheme 10. Mechanism for alkyl exchange.

XIV. HYDROSILYLATION/GERMYLATION REACTIONS

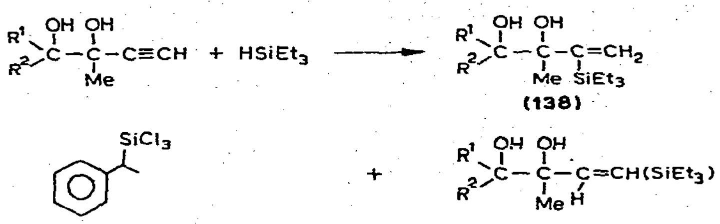
In the presence of PPh_3, palladium compounds PdX_2 ($X = Cl, OAc$), and Pd metal are all active hydrosilylation catalysts for olefins and dienes with $HSiCl_3$ and $HSiMe_3$[325]. $HSiCl_3 > HSiMe_3$ and conjugated dienes > 1-olefins > inner olefins have been presented as the orders of reactivity[325]. Use of $Pt(PPh_3)_4$ as catalyst leads to hydrosilylation of terminal olefins (but not internal olefins) without isomerization for $HSiCl_2Me$[326].

The widely used Speier's catalyst for hydrosilylation ($H_2PtCl_6{\cdot}6H_2O$ in Me_2CHOH) has been found to contain acetone, HCl, and some Pt^{II} suggesting the reaction[327]

$$H_2PtCl_6 + Me_2CHOH \rightarrow H_2PtCl_4 + CH_3COCH_3 + 2HCl$$

The hydrosilylation of di-tert-acetylenic-α-glycols with this catalyst yields two products assigned by spectral data to (138), (139)[328]. $[Cl_2Pt(HC{\equiv}CCMe_3)]_2$ in i-PrOH has been reported as a better catalyst than Speier's catalyst[329,161]. Butadiene hydrosilylation has been reported for several Pd and Ni catalysts[330].

Use of $Pt(C_2H_4)L_2$ ($L = PPh_3$) as a hydrosilylation catalyst gave good conversion of



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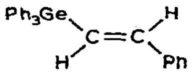

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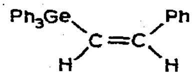

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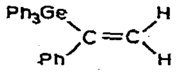


(143)

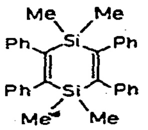
terminal olefins with a variety of silanes without appreciable isomerization[331]. Several complexes were isolated from these systems[331].

The square planar $NiCl_2 \cdot (P\text{-}n\text{-}Bu_3)_2$ complex was found to be a more active catalyst than the tetrahedral $NiBr_2(PPh_3)_2$ for the reaction of styrene + $HSiCl_3$[332]. $Ni[P(OPh)_3]_4$ was found to equal the best previously known Ni^0 catalyst. Addition of CuCl to this type of system dramatically increased the yield of products, which were predominantly the α adduct (**140**)[332].

Hydrogermylation of PhC≡CH leads to products in the proportions (**141**) ≫ (**142**) ≫ (**143**) for the catalysts $H_2PtCl_6 \cdot 6H_2O$ and *cis*-$(PPh_3)_2PtCl_2$ with retention of configuration at the germanium center for HGe*Ph(Me)Np[333].

Addition of $HSiMeCl_2$ to α-methylstyrene using *trans*-dichlorobis[(*R*)-benzylmethylphosphine] nickel(II) with $^*PR_3$ of optical purity 81% gives a product dichloromethyl(2-phenylpropyl)silicon with about 17.6% optical purity[334]. Asymmetric hydrosilylation has been reported also with *cis*-$(C_2H_4)^*PR_3PtCl_2$ and $(R_3^1P^*PtCl_2)_2$ for the addition of $HSiCl_2Me$ to α-methylstyrene and to 2-methyl-1-butene[335]. The results were poorer than for the nickel complex above with about 5% (*R*) enantiomeric excess for the first catalyst with $PhMeC{=}CH_2$ and less for the second catalyst. The butene gave only 0.9% bias towards the (*R*) isomer for the first catalyst and less for the second[335].

Disproportionation of $Me_3SiSiMe_2H$ catalyzed by *trans*-$PtCl_2(PEt_3)_2$ has been proposed to proceed via α-elimination to give "dimethylsilylene" (perhaps from a metal complex of $Me_3SiSiMe_2H$) which can be trapped by PhC≡CPh to give $2Me_3SiH$ and (**144**)[336].



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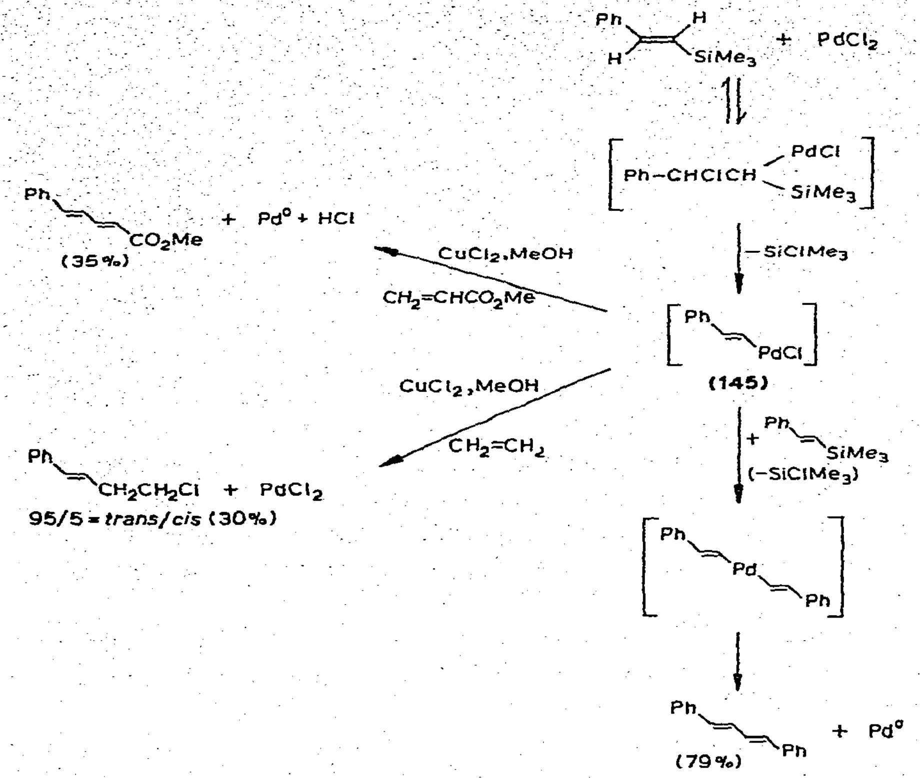
Dehydrocondensation of phenol and silane is catalyzed by several Ni, Pd, Pt compounds and by the metals in certain physical states[337] *e.g.*:

$$R_3SiH + PhOH \xrightarrow{\text{catalyst}} R_3SiOPh + H_2$$



Scheme 11. Interaction of vinylsilane with PdCl$_2$

Extension of the catalytic reaction using dihydric phenols and dihydrosilanes in bulk or in a solvent at $> 150°$ gave high molecular weight polymers containing a Si–O–phenylene linkage in the main chain[337].

The interaction of vinylsilanes with PdCl$_2$ has led to reactions which might be expected for vinylpalladium species such as (**145**)[338]. (A summary of reactions is shown in Scheme 11).

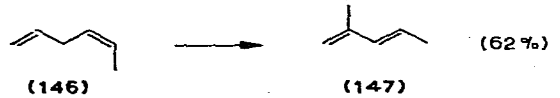
XV. OTHER SYNTHETIC AND CATALYTIC REACTIONS INVOLVING Ni, Pd, Pt

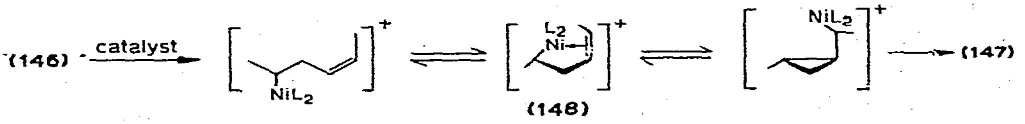
A. Nickel

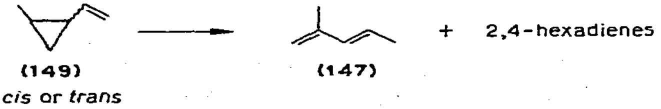
Homogeneous hydrogenation of eight-membered cycloolefins has been carried out using *o*- and *p*-dihydroxybenzene as hydrogen donors and Ni(PPh$_3$)$_2$X$_2$ ($X = I > Br \geqslant Cl$) as catalyst[339]. Hydrogenation of oxygen containing unsaturated compounds by nickel boride occurs quantitatively without rearrangement, hydrogenolysis, or carbonyl reduction[340]. The catalyst system n-BuLi–nickel octanoate has been found to be less active than the related cobalt system for hydrogenation of cyclooctene[341].

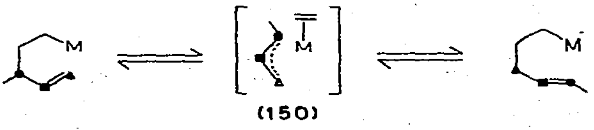
The reduction and rearrangement of butadiene by aqueous Ni(CN)$_6{}^{2-}$ has been studied kinetically and two distinct reaction intermediates (a π-allylic species and π-diene species) have been proposed to account for the production of *trans*- and *cis*-butene[342]. The presence of nickel ions on 13X-type zeolites enhances the catalytic rearrangement of n-butene to *trans*-2-butene (probably via radical intermediates)[343]. Detailed analysis of the exchange products of the reactions of D_2 and 1-butene over NiX catalysts to yield butane shows that exchange is comparable to isomerization and that hydrogenation is accompanied by a substantial redistribution of H and D[343]. Supported acid metal salts isomerize butene with activity and selectivity (*cis*/*trans*) increasing with the acid strength of the catalyst[344]. These observations were explained by a mechanism involving a sec-butyl carbonium ion[344].

Skeletal rearrangement of dienes promoted by systems which presumably give nickel hydride species, ($[(o\text{-tolyl})_3P]_3Ni$ and HCl in THF), results in conversion of (146) to (147) via the proposed intermediate (148)[345]. Similar systems including $[P(o\text{-tolyl})_3]_2NiC_2H_4$ + HCl rearranged (146) to (147) (74% conversion in 2.5 min) and (149) to (147)[346]. Miller *et al.* have discussed the mechanisms of nickel complex catalyzed rearrangement of the types; 1,4-pentadiene to isoprene and 3-methyl-1,4-pentadiene to 1,4-hexadiene[347]. The reaction mechanism of the latter rearrangement has been shown to occur via intermediate (150)[347].



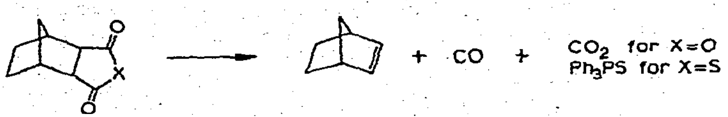






H/D exchange between C_2D_4 and C_2H_4 in the presence of H_2 and $NiX_2(PPh_3)_2$ occurs via a hydrido intermediate[348]. Bis(*N*,*N*-diethyldithiocarbamato)nickel will catalyze the exchange of halogens in α,α'-dibromo-*o*-xylene in refluxing CH_2Cl_2 forming α,α'-dichloro- or α,α'-bromochloro-*o*-xylene[349].

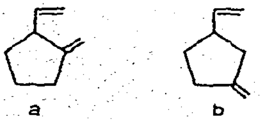
Direct thermal reaction of $Ni(COD)_2$ and aryl halides ($I > Br > Cl$) in DMF has been found to be a satisfactory route to certain biaryls[350]. Methylation at the *ortho* position in phenols at 350° was performed by the nickel oxide–ferric oxide catalyst with gasification of methanol taking place simultaneously as a side effect[351]. The effect that addition of various metal chloride salts to a stabilized nickel catalyst has on the ratio of benzene, toluene, and benzaldehyde produced from benzyl alcohol has been documented[352]. 2-Cyanopyridine has been catalytically hydrated to 2-pyridinecarboxamide using Ni(En)$_3$-Cl$_2$·2H$_2$O, and Ni(L–L)$_2$Cl$_2$·2H$_2$O (L–L) = 2-pyridinecarboxamide)[353]. (PPh$_3$)$_2$Ni(CO)$_2$ mediates the elimination of anhydrides from compounds like **(151)** to give the corresponding olefin (53%)[354]. Acidic metal sulfates including the nickel salt on silica gel at 300° dehydrohalogenate haloethanes with activity and selectivity correlating with the electronegativity of the metal[355].



X = S,O
(151)

Polymerization of phenylacetylene has been studied for a variety of Ni^{II}, Pt^{II} complex catalysts by analysis of the reaction products and ESR spectroscopy[356]. The spectrum of stable paramagnetic species present in the polymeric fractions of the reaction products and of transient species formed during the reaction have been observed. A mechanism based on insertion of monomer into the σ-metal–carbon bond has been proposed on the basis of the results obtained[356]. Nickel complexes such as Ni(MeCOCHCO$_2$Et)$_2$ will convert acetylene to H$_2$C=CHC≡CH at 80° in Py[357]. The most effective catalysts for the dimerization of butadiene to **(152)** (in the presence of ROH) were (Bu$_3$P)$_2$NiX$_2$/LiR, (*o*-tolyl)NiX(PEt$_3$)$_2$ and (π-allylNiBr)$_2$ + P-n-Bu$_3$ [358]. For the arylnickel catalyst CH$_3$OD has been found not to deuterate the toluene which is reductively cleaved from the nickel before dimerization occurs. CD$_3$OD on the other hand gives monodeuterated toluene. The cyclodimerization is thought to involve a hydrogen migration from the protic compound.

Oligomerization of butadiene by electrolytically reduced nickel species has been described in two publications[359,360]. Oligomerization during the electrolysis of solutions containing NiCl$_2$ and electron donors depends on the nature of that donor. When Py was used (with or without the presence of electrolyte) a number of linear and dihydrogenated oligomers along with a small amount of branched oligomers were obtained. When PPh$_3$ was used n-octatriene and alkoxy octadiene were catalytically produced and accompanied by formation of (PPh$_3$)$_4$Ni. A mechanism involving **(153)** and **(154)** has been discussed[359]. Electrolytic reduction of NiCl$_2$/PPh$_3$ or (PR$_3$)$_2$NiCl$_2$ will give catalysts for the conversion of butadiene to 4-vinylcyclohexene and COD[360]. Addition of Diphos yielded (89%)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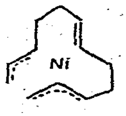
(152)

(153)



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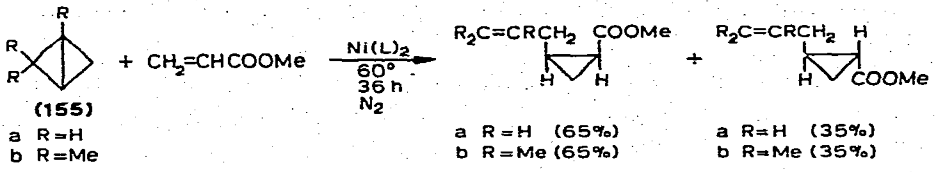
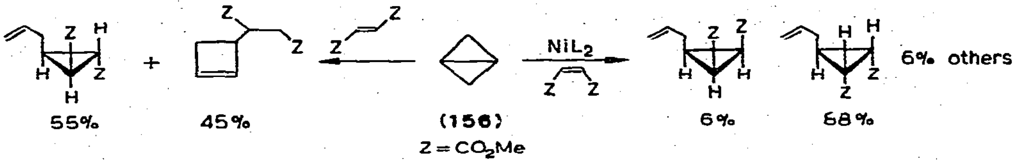
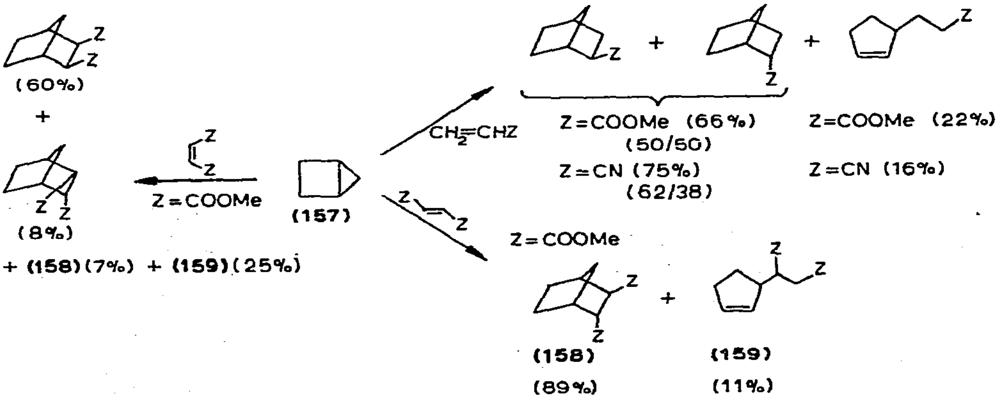


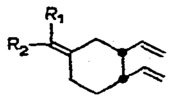


(Diphos)$_2$Ni suggesting a Ni^0 species is present in the electrolytic reduction. Acetonitrile and DMF were the solvents best suited to the reaction.

Bicyclo[*n*.1.0] alkanes react with olefins (for *n* = 1, 2) to give different products under the mediation of bis(acrylonitrile)nickel(0) than under thermal reaction[361]. Representative reactions are illustrated for *n* = 1 **(155) (156)**[361] and *n* = 2 **(157)**[362]. A rationale for the products in *n* = 2 cases has been advanced.

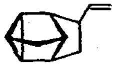
Reaction of (1/10) allene/butadiene in an autoclave with tris(2-biphenylyl)phosphite nickel(0) gives 35% of 8- and 9-methylene-*cis,trans*-1,5-cyclododecadiene[363]. 1,1-Dimethylallene or methoxyallene and butadiene with nickel catalysts (Ni^0–L) afforded the analogous products which were isolated after Cope rearrangement to **(160)**[363]. Reaction of butadiene and amines (primary and secondary) gives octadienyl and butenyl substituted amines by utilization of catalysts which produced nickel(0) species[364]. A similar catalytic





(160)

R^1 = R^2 = CH$_3$ (45%)
R^1 or R^2 = OMe, R^2 or R^1 = H (40%)



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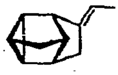


(162)

system telomerized butadiene with alcohols to give 2,7-octadienyl ethers as the major products[365].

$AlEt_3$ used with $NiCl_2$ or $Ni(Acac)_2$ will isomerize α-olefins to internal *cis,trans* olefins[366]. Dimerization of propene by a variety of these systems has been undertaken by Jones who has reported the production of about 30% n-hexene and 70% methylpentene at reaction temperatures of 40–80°. (Higher temperatures favour n-hexene formation)[367]. Propene and other 1-olefins dimerize with $Ni(Acac)_2$—$AlEt_2(OEt)$ to linear dimers with a selectivity of 75–80%[368]. Solvent influence on the polymerization of acetylene by $NiCl_2/Al\text{-}i\text{-}Bu_3$ was studied[369]. Oligomerization of butadiene by $Ni(Acac)_2/Al(OEt)Et_2$ to cyclic olefins and with $AlBr_3$ or $HOOCCF_3$ to polybutadienes has been reported[370]. $Ni(PCl_3)_4/AlBr_3/BuLi$ dimerizes C_2H_4, isomerizes 1-butene and codimerizes C_2H_4 and styrene[371]. The $NiCl_2/AlClEt_2/2PPh_3$, Or $Ni(Acac)_2/AlEt_2Cl$ systems codimerize NBD and butadiene to give small yields (relative to the NBD introduced) of **(161)** and **(162)**[372].

$BF_3{\cdot}Et_2O$ has been used as a co-catalyst with $(PPh_3)_2Ni(\sigma\text{-}Np)Br$ in dry CH_2Cl_2[373]. The system exchanges H/D in C_2H_4 and C_2D_4 whilst dimerizing ethylene at a much slower rate. Co-dimerization of C_2H_4 and styrene occurs also with this catalyst[374].

B. Palladium

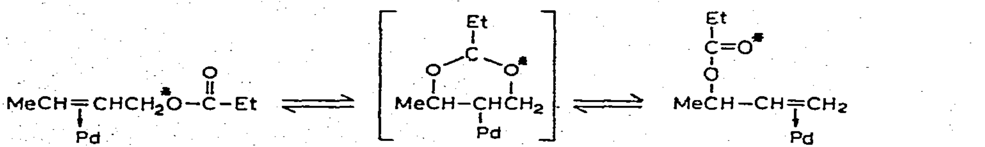
A review of addition and elimination reactions of palladium complexes with olefins written by Heck has been published[375].

$PdCl_4^{2-}$ on a basic ion exchange resin will hydrogenate olefins in alcoholic solution at 25°[376]. The activity and kinetic behaviour differs from that of metallic palladium and $PdCl_4^{2-}$ does not act as a catalyst in the absence of a co-catalyst[376].

A novel allylic isomerization pathway has been proposed by Henry for Pd^{II} catalyzed reactions of the type:

$$MeCH{=}CHCH_2OOCEt \xrightleftharpoons{Pd^{II}} Me(OOCEt)CHCH{=}CH_2$$

By ^{18}O labelling it was found that alcohol oxygen of the 2-butenyl propionate becomes the carbonyl oxygen of 1-buten-3-propionate[377]. This observation along with data on exchange reactions led to a mechanism with a 1,3-acetoxonium type ion intermediate **(163)**[377].



(163)

Henry has studied the Pd^{II} catalyzed *cis/trans* isomerization of enol propionates (and vinyl halides) and has found that it occurs without exchange reactions and is consistent with the kinetic expression[378]:

$$k = \frac{k[\mathrm{Li_2Pd_2Cl_6}]\,[\text{enol propionate}]}{[\mathrm{LiCl}]}$$

On the basis of his observations the author has eliminated reactions via π-allylic or hydridic intermediates. A π-complex intermediate is consistent with the data[378]. Pd^{II} catalyzes exchange:

$$\mathrm{CH_2{=}CHOOCCD_3} \xrightleftharpoons[\mathrm{HOOCCD_3}]{\mathrm{HOOCCH_3}} \mathrm{CH_2{=}CHOOCCH_3}$$

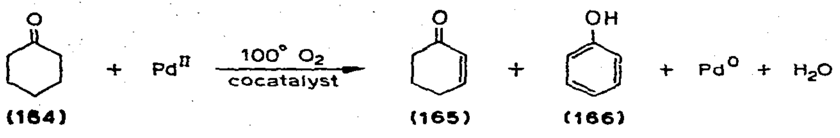
For 1-acetoxy-1-propene exchange occurs only with *cis/trans* isomerization and kinetic and stereochemical results have led to the proposal of a mechanism:

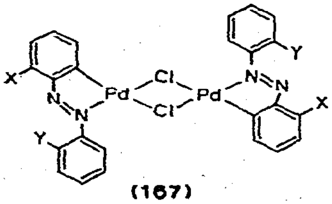
$$\mathrm{C_2H_3OOCCD_3} + -\overset{|}{\underset{|}{\mathrm{Pd}}}\mathrm{OOCCH_3} \rightarrow -\overset{|}{\underset{|}{\mathrm{Pd}}}\mathrm{CH_2CH(OOCCD_3)(OOCCH_3)} \rightarrow$$

$$-\overset{|}{\underset{|}{\mathrm{Pd}}}\mathrm{OOCCD_3} + \mathrm{C_2H_3OOCCH_3}$$

Consistent with this mechanism is the non-reactivity of cyclic enol acetates and the inhibition of the process on vinyl substitution[379].

Cyclohexene, 1,5-cyclohexadiene, or 1,4-cyclohexadiene react rapidly with $Pd(OAc)_2$ to form benzene but the reaction depends on the presence of some elemental Pd^0 being formed in the reaction[380]. Preparation of α,β-unsaturated aldehydes and ketones from the corresponding saturated aldehydes or ketones has been carried out by an oxidative dehydrogenation by air or oxygen in the presence of $Pd(PPh_3)_2Cl_2$ and a co-catalyst such as $Cu(PPh_3)_2Cl_2$ or a quinone in $HOOCR$[381]. 15–30% conversion of **(164)** gave 80–95% selectivity to **(165)** which converts slowly to **(166)** when in continued contact with metallic palladium[381].





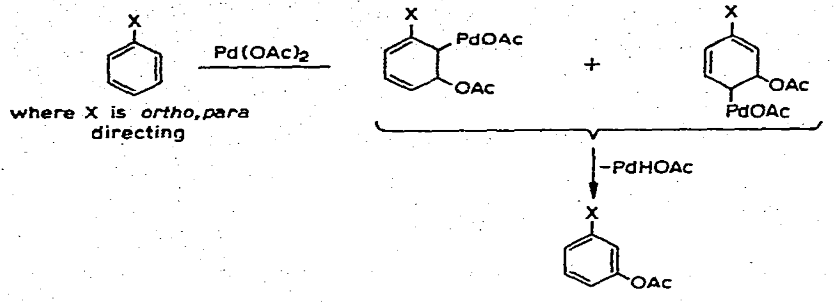
(167)

X=Y=H,Cl

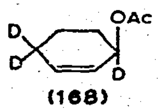
ortho-Halogenation products of azobenzene, (as in the conversion of 2-chloroazobenzene to 2,6,2′,6′-tetrachloroazobenzene), result from the reaction of Cl_2 (or Br_2) with an isolable intermediate (167) formed from azobenzene and the catalyst $PdCl_2$[382].

Elemental palladium on a silica support has been found to oxidize CO in a process promoted by hydrogen[383]. In the palladium-catalyzed synthesis of vinyl acetate from ethylene, $Pd(OAc)_2$ was formed under conditions of high partial pressures of HOAc and O_2 and at low temperatures[384].

Acetoxylation of unsaturated substrates can be carried out in the presence of Pd^{II} compounds. $Pd(OAc)_2$ nuclear acetoxylation of aromatic compounds containing *ortho,-para*-directing substituents gave *meta*-acetoxy-products[385]. A rationale for this reversal of orientation pattern in the products has been suggested (Scheme 12)[385]. The reaction of isoprene with HOAc catalyzed by $PdCl_2$ + NaOAc and an electron donor (PPh_3) has been studied with respect to the reaction products under various conditions[386]. The use of non-polar solvents yielded isoprene monomer acetates as the main products while polar solvents favoured isoprene dimer acetates[386]. Two groups of researchers have reported investigation of the mechanism of acetoxylation of cyclohexene and deuterium labelled cyclohexene in the presence of Pd^{II} and a co-catalyst ($CuCl_2$[387] and HNO_3, HNO_2, or $Hg(OAc)_2$[388]) in HOAc. Both studies found that the reaction led to a 1/1 mixture of acetates (168) and (169). A competing though less important reaction is the formation of (170). Synthesis and reaction of π-cyclohexene and π-allylic cyclohexenyl



Scheme 12. Mechanism for *meta*-acetoxylation.



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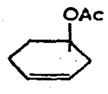

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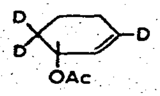
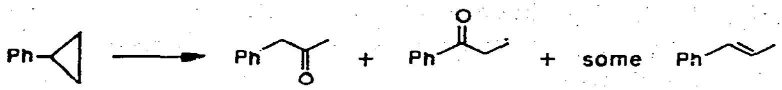


(169)

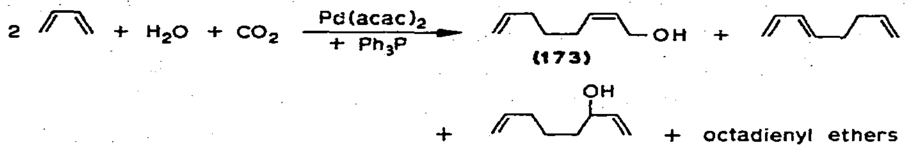
model compounds were carried out and found to support the intervention of monomeric π-allylic intermediates in the above allylic oxidations[389].

A catalytic conversion of olefins to ketones in high yields has been developed involving the addition of a methanol solution of $Hg(OAc)_2$ and olefin to a solution of $PdCl_4^{2-}$ and $CuCl_2$ (followed by hydrolysis with $NaHCO_3$)[390].

The oxidation of (**172**) by Na_2PdCl_4 in 2/1 glyme/H_2O gives propiophenone (**171b**) and phenylacetone (**171a**); the former favoured by large amounts of catalyst[391].



(172) a (171) b



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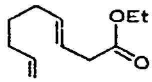
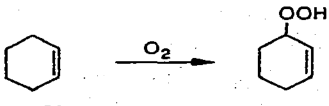
(174)



(175)

Butadiene with (Pd(Acac)$_2$ + PPh_3) catalyst reacts with H_2O in the presence of CO_2 to give high yields of the octadienols (**173**) along with other dimeric alcohols (**174**), ethers and dimers[392]. A similar carbonylation dimerization of butadiene in the presence of (Pd(Acac)$_2$ + PPh_3) and CO and EtOH gives (**175**) along with ethoxyoctadienes[393]. Substituted conjugated dienes may be carbonylated with CO in alcohol using $PdCl_2$ catalyst to give unsaturated esters as the general product[394]. Allyl alcohols with $PdCl_2$ and H_2O give allylic ketones and aldehydes (after dehydration of the initial products with acid)[395]. $PdCl_2$ is reported to catalyze insertion of CO into a nitrogen–chlorine bond in the conversion of chloramine to carbamoyl chloride[396]. EtOH and CO react under the influence of LiCl + $PdCl_2$ to give ethyl chlorocarbonate and ethyl acetate, together with Pd and an unidentified compound[397].

In the case of the autooxidation of cumene at 35° catalyzed by $(PPh_3)_4Pd$, chain initiation has been attributed to decomposition of the hydroperoxide still present in the cumene and not to oxygen activation by the transition metal[398]. A similar conclusion has been reached in the oxidation of cyclohexene (**176**) catalyzed by $(PPh_3)_2PtO_2$ or $(PPh_3)_3Pt$ at 65° and 1 atmosphere O_2[399]. The process does not involve oxygen activa-

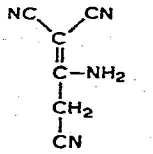


(176)

tion by the platinum. The effective action of the transition metal has been attributed instead to its interaction with preformed cyclohexene hydroperoxide to form radicals[399].

It has been previously reported that reaction of butadiene with malononitrile, catalyzed by platinum complexes, gives only a small amount of 2,7-octadienyl derivatives and a large amount of yellow solid which has now been identified as (177)[400]. Methyl acrylate reacts with $PdCl_2 - NaOAc$ in HOAc at 100° to give a low yield (4.6%) of trimer along with small amounts of other aromatic products[401]. Pd^{II} catalysis of butadiene oligomerization gave different products depending (i) on whether or not the anions present were non-complexing (ClO_4^-) or complexing (Cl^-, RCO_2^-), (ii) on the nature of added electron donors (PPh_3) and (iii) on the solvents[402,403].

Arylation of olefins involving palladium compounds is an area of active interest. Phenylation of $[\beta,\beta\text{-}^2H_2]$ styrenes with benzene in the presence of $Pd(OAc)_2$ in HOAc was found to give *trans*-stilbenes without a hydride shift occurring[404]. The same sort of reaction was achieved for benzene or toluene on reaction in refluxing HOAc with the previously prepared α-olefin–palladium(II) complexes (178) and AgOAc[405]. The reaction of benzene with either *cis*- or *trans*-(β-chlorovinyl)palladium(II) complex (178) led to *trans*-β-chlorostyrene in high yield. The use of mild oxygen pressure has been reported to make the coupling of styrenes (or ethylene) and benzene in the presence of $Pd(OAc)_2$ a catalytic process by preventing the reduction of the catalyst[406]. The reaction of PhI with olefins in the presence of ($PdCl_2$/KOAc) was found to be catalytic and proceeded as follows[407]:



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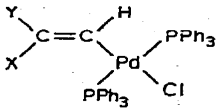


(178)

Y = X = Cl
Y = Cl, X = H
Y = H, X = Cl

$$PhI + CH_2{=}CHX + KOAc \rightarrow PhCH{=}CHX + HOAc + KI$$

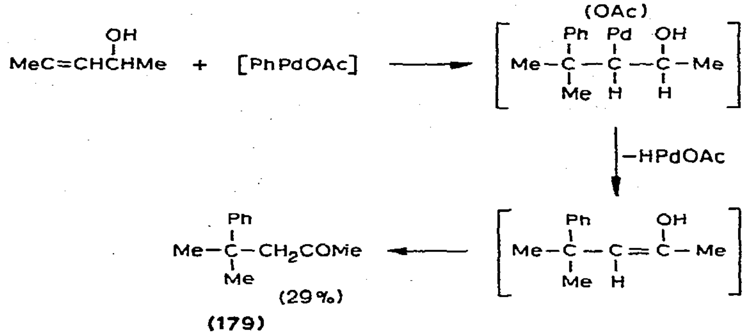
$$X = H, Ph, Me, COOMe$$

A significant kinetic isotope effect has been observed for the phenylation of styrene with benzene or benzene-d_6 in the presence of $Pd(OAc)_2$:

$$C_6H_6 + C_6D_6 + PhCH{=}CH_2 + Pd(OAc)_2 \rightarrow$$

$$trans\text{-}PhHC{=}CPhH + trans\text{-}PhCH{=}CH(C_6D_5) + Pd^0 + HOAc + DOAc$$

For this reaction $K_H/K_D = 5.0$, and suggests that Pd—aryl σ-bond formation is the slow, irreversible step in the reaction[408]. The course of arylation and carboalkoxylation of olefins with aryl and carboalkoxypalladium compounds to form styrenes and unsaturated esters respectively has shown that in general addition is sterically controlled with the larger organic group adding to the least substituted olefinic carbon and the palladium group adding to the most substituted even though electronically the organic group prefers the more positive center[409]. In some appropriately substituted olefins chelating interaction may direct the organic group to the most substituted carbon against steric and electronic controls. Such chelating effects have been noted in the arylation of various methyl-substituted allylic alcohols where 3-aryl carbonyl compounds are formed (179)[409].

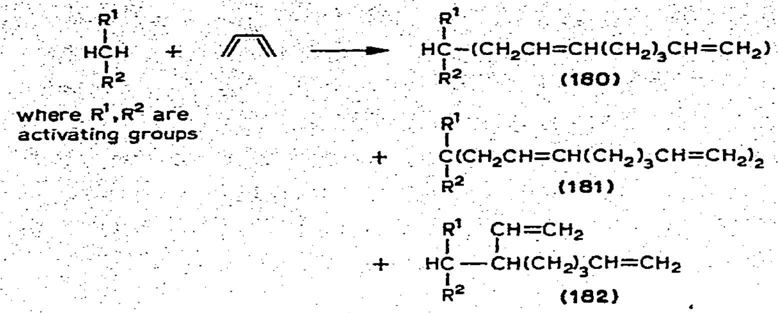


(179)

Alkylation or arylation of mono- or di-substituted ethylenes by methylcobalamine and related organocobalt chelates in the presence of Li_2PdCl_4 at 20–50°. Allylcobalt compounds under the same reaction conditions give stable π-allyl palladium derivatives[410,411].

In the $PdCl_2L_2$ ($L = NH_3$, Py, PPh_3, $AsPh_3$)–basic salt, $Pd(PPh_3)_4$, $PdCl_2$–basic salt and $Pd(NO_2)_2(NH_3)_2$–basic salt catalyzed reaction of active methylene compounds with 1,3-butadiene, (180) and (181) were the main products with some (182) being formed[412,413]. Reactions with isoprene give the derivatives of a tail to tail dimerization while 1,3-pentadiene results in a head to tail dimerized adduct. The platinum systems $[PtCl_2(PPh_3)_2–NaOPh]$ and $[Pt(PPh_3)_4–NaOPh]$ were also used as catalysts. Formation of (182) was observed along with 1/1 and 1/3 adducts as well as (180) (a 1/2 adduct) and (181) (a 1/4 adduct). The intermediate (183) has been suggested[412,413]. Co-dimerization of styrene with vinyl compounds is catalyzed by $(styrene)_2Pd_2Cl_4$ under mild conditions when the vinyl compounds are $CH_2{=}CHX$ (X = COOMe, OAc, C(O)Me)[414]. A mechanism is proposed in wich a hydride shift occurs between *cis*-coordinated styrene and coordinated vinyl groups in an intermediate palladium complex (184)[414]. Oxidative coupling of toluene or xylenes in a mixture of $CH_3COCH_2COCH_3$ and $Pd(OAc)_2$ heated under O_2 pressure gives biphenyls in the yields toluene > *o*-xylene > *m*-xylene > benzene > *p*-xylene[415].

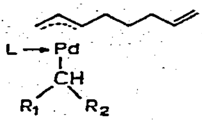
Butadiene and RCO_2H with a $PdCl_2$, $CuCl_2$ catalyst gave crotyl and methyl allyl ester[416]. $Pd(OAc)_2$ and PPh_3 catalyzed the reaction of butadiene with ammonia in acetonitrile to yield tri-2,7-octadienylamine[417]. Similarly 1-nitropropane and butadiene with a $(PPh_3)_2PdCl_2/NaOPh$ catalyst in n-BuOH gave (185) and (186)[417]. Conjugated dienes on reaction with isocyanate gave divinylpiperidones via a 2/1 cyclization when using



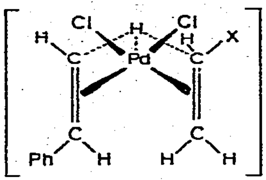
(180)

(181)

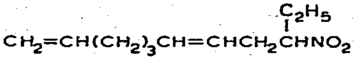
(182)



(183)

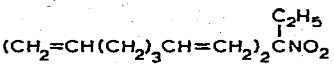


(184)



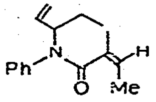
$CH_2{=}CH(CH_2)_3CH{=}CHCH_2\overset{C_2H_5}{\overset{|}{C}}HNO_2$

(185)

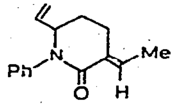


$(CH_2{=}CH(CH_2)_3CH{=}CH_2)_2\overset{C_2H_5}{\overset{|}{C}}NO_2$

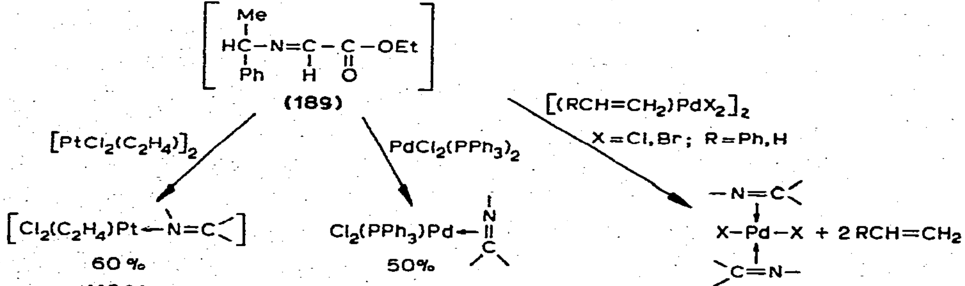
(186)



(187)



(188)

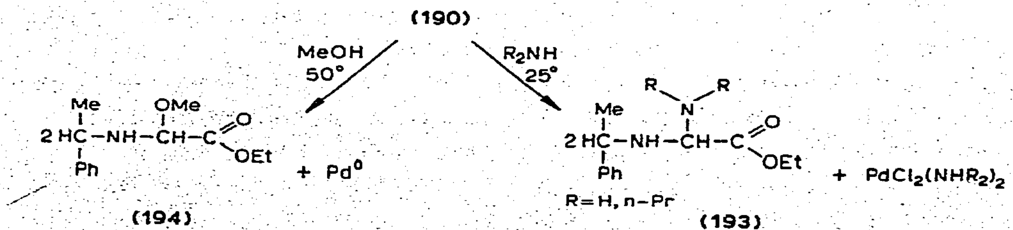


(189)

(192)

(191)

(190)



(190)

(194)

(193)

$Pd^{II}(PPh_3)$ catalysts[418]. For the reaction involving 1,3-butadiene and PhNCO equal amounts of (187) and (188) were generated[418].

Reaction of (189) with metal compounds gives the complexes (190), (191), (192). Reaction of (190) with nucleophiles R_2NH and MeOH gave (193) and (194) respectively[419].

C. Platinum

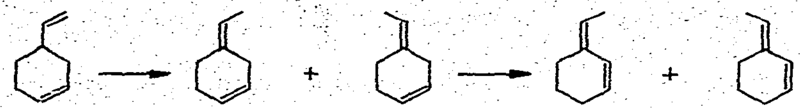
The initial rates of hydrogenation of acetylene and ethylene catalyzed by methanolic $Pt^{II}/SnCl_2$ systems are given by an expression

$$\text{Initial rate} = kK_{HC}P_{HC}P_H/(1 + K_{HC}P_{HC})$$

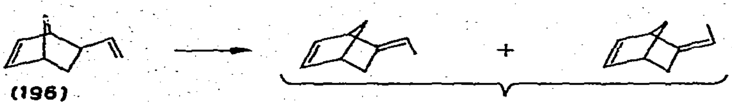
where k, K_{HC} are constants, P_{HC} is the pressure of hydrocarbon and P_H is the pressure of hydrogen. The initial rates exhibit maxima at a particular Sn/Pt ratio present[420]. Acetylene is consecutively hydrogenated to ethylene then ethane with little incorporation of deuterium when D_2 is employed. Exchange of deuterium in the hydrogenation of C_2D_2 to predominantly *cis*-$C_2D_2H_2$ with H_2 is hardly observed whereas the exchange proceeds considerably in the case of the hydrogenation of C_2D_4. The results have been interpreted in terms of a heterolytic cleavage of the hydrogen, competitive coordination of C_2H_2 and C_2H_4 and successive reactions with hydride and protonic hydrogens.

H/D exchange in alkanes has been observed for the catalyst K_2PtCl_4 in a CH_3CO_2D/D_2O solution containing $DClO_4$, pyrene, and an alkane. Homogeneous catalysis exchanged the protium in the alkanes for deuterium from the solvent with the rate of primary C—H > secondary C—H > tertiary C—H[421]. The exchange is preceded by dissociation of Cl^- ligands to give a neutral Pt^{II} species and is related to the ionization potential of the n-alkane C—H bonds. Cycloalkanes are more reactive than n-alkanes. The exchange mechanism has been suggested to include the oxidative addition of alkane to platinum to give a hydride species[422]. Deuteration in the side chain in long chain alkylbenzenes using Na_2PtCl_4, CH_3CO_2D, D_2O and DCl at 120° occurred primarily at the α- and terminal carbon positions with isotope incorporation progressively decreasing from n-butyl to n-nonylbenzene[423]. H/D exchange in polycyclic aromatic hydrocarbons in heterogeneous and homogeneous systems leads to identical deuteration patterns and may be divided into two classes of compounds; condensed polycyclics and polyphenyls[424]. With the first group, initial deuteration is exclusively stepwise and to the β- or equivalent position. In polyphenyls multiple deuteration occurs, with exchange occurring one ring at a time in the *meta*- and *para*-positions. The authors have suggested from their results that homo- and heterogeneous catalysis in these systems is by an analogous π-complex mechanism. The system was observed by EPR techniques[424].

The $PtCl_2(PPh_3)_2$—$SnCl_2$ system under hydrogen pressure in methanolic solution (or aprotic solvent solution) will isomerize vinylcycloalkenes (195) to four products (65% yield). Isomerization of (196) was also carried out to give 40% of (197) when 61% isomerization had taken place[425].



(195)



(196)

(197)

Reduction of olefins and acetylenes by formic acid and formates proceeds slowly with platinum metal catalysts. (H_2PtCl_6–$SnCl_2$) and *cis*-$(PEt_3)_2PtCl_2$ both show some small activity at 100° toward the reduction of 1-octene to octane[426].

The oxidation of CO by Fe^{3+} in the presence of $Pt(CO)(HX)_2$ ($X = Cl, Br, I$) depends on the concentration of [Pt] and [CO] but not on $[Fe^{3+}]$[427].

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