NICKEL, PALLADIUM AND PLATINUM ANNUAL SURVEY COVERING THE YEAR 1977

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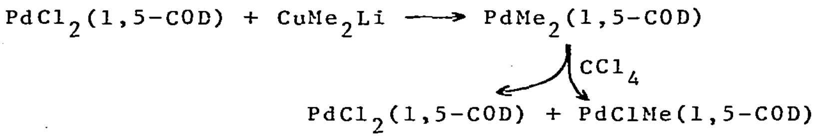
ABBREVIATIONS

dpm	bis-1,2-(diphenylphosphino)methane	OAc	acetate
dpe	bis-1,2-(diphenylphosphino)ethane	acac	acetylacetonate
dpp	bis-1,2-(diphenylphosphino)propane	NBD	norbornadiene
dpb	bis-1,2-(diphenylphosphino)butane	1,5-CoD	1,5-cyclooctadiene
py	pyridine	cp	cyclopentadienyl
bipy	2,2'-bipyridyl	THF	tetrahydrofuran
phen	1,10-phenanthroline		

Nickel, Palladium and Platinum, Annual Survey Covering the Year 1976, see <u>J. Organometal. Chem.</u>, 147 (1978) 335.

I. Metal-carbon σ complexes

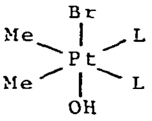
The complex $PdMe_2(1,5\text{-}COD)$ (1) has been prepared by treating $PdCl_2(1,5\text{-}COD)$ with the reagent $CuMe_2Li$. The complex poorly alkylates olefins. The complex $PdClMe(1,5\text{-}COD)$, obtained by treating $PdMe_2(1,5\text{-}COD)$ with CCl_4, will alkylate styrene [1]. Dialkyl palladium(II) complexes have also been obtained by treating $Pd(acac)_2$ with $AlR_2(OEt)$ in the presence of a tertiary phosphine [2]. The following complexes are reported: $PdR_2(PEt_3)_2$, $PdR_2(PPh_2Me)_2$, $PdR_2(dpe)$ (R = Me, Et, *n*-Pr). Anhydrous pure $PtMe_3ClO_4$ (2) has been prepared by treating $PtMe_3I$ with $AgClO_4$. The complex is moisture and shock sensitive [3]. Spectroscopic and preliminary X-ray data indicate a tetrameric structure. Solutions of the complex ion $[PtBrMe_2(H_2O)_3]^+$ have been prepared by treating the compound $[PtBr_2Me_2]_n$ with aqueous silver ion. This complex reacts with neutral donor ligands such as 3,5-lutidine or N,N,N',N'-tetramethylethylenediamine, or anionic ligands such as Br^-, Cl^-, I^-, OH^-, SCN^- and NO_2^-. The major effort is devoted to solution work but the complex $PtBr(OH)Me_2(3,5\text{-lutidine})_2$ (3) has been isolated from treating $[PtBrMe_2(H_2O)_3]^+$ with 3,5-lutidine [4]. The dithiocarbamate complexes $[PtMe_3(S_2CNR_2)]_2$ ($R_2 = Me_2, Et_2, (CH_2)_4$) are stereochemically rigid in solution in contrast to the xanthates $[PtMe_3(S_2COR)]_2$ (R = Me, Et, *i*-Pr) which are non-rigid above -40° C [5]. An alkyl platinum(IV) complex (4) has been prepared by treating $(PtMe_3)_2SO_4\cdot 2H_2O$ with thiooxine in aqueous chloroform. The compound



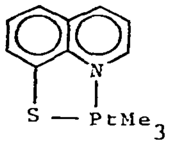
$$PdCl_2(1,5\text{-}COD) + CuMe_2Li \longrightarrow PdMe_2(1,5\text{-}COD) \xrightarrow{CCl_4} PdCl_2(1,5\text{-}COD) + PdClMe(1,5\text{-}COD) \qquad (1)$$

$$PtMe_3I + AgClO_4 \longrightarrow PtMe_3ClO_4 + AgI$$

(2)



(3)(L = 3,5-butidine)



(4)

is extracted by chloroform [6]. The anion $PtMe_6^{2-}$ has been prepared from treating $[PtMe_3I]_4$, $[PtMe_3Cl]_4$ or $PtMe_4(PPh_2Me)_2$ with $[LiMe]_4$ in THF [7]. Raman and ^1H NMR spectra are consistent with an octahedral species. The compound $Li_2[PtMe_6]$ (5) reacts with MeI to give $Li_2[PtMe_3I_3]$.

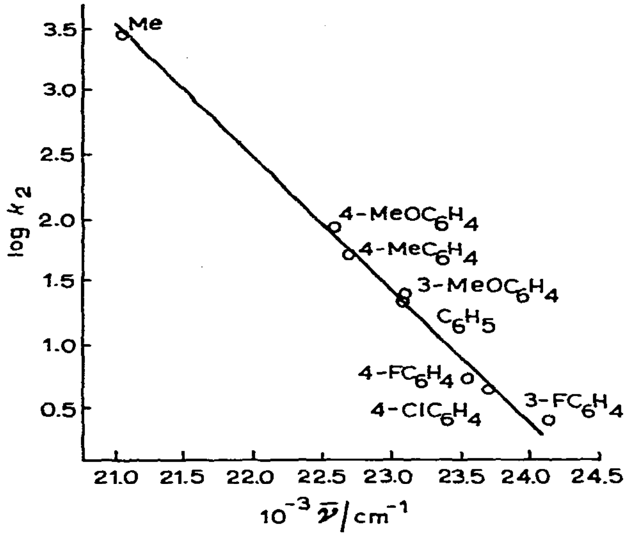
$$[PtMe_3I]_4 + [LiMe]_4 \longrightarrow Li_2[PtMe_6] \xrightarrow{MeI} Li_2PtMe_3I_3$$

(5)

Five coordinate nickel(II) compounds $[NiR(L)]BPh_4$ (L = tris(2-diphenylphosphinoethyl)amine, tris(2-diphenylarsinoethyl)amine, tris(2-diphenylphosphinoethyl)phosphine; R = Me, Et, benzyl) have been prepared from the corresponding halo compounds and a Grignard reagent [8]. The crystal structure of the methyl complex with the amine ligand (6) shows a trigonal bipyramidal arrangement about the metal center with the methyl group in the axial position. Dimethyl platinum(II) complexes of the three triphosphines $PhP(CH_2CH_2CH_2PPh_2)_2$, $PhP(CH_2CH_2PPh_2)_2$ and $PhP(CH_2CH_2PMe_2)_2$ have been shown by ^{31}P NMR to exchange the terminal phosphino groups. A mechanism involving a five-coordinate intermediate is favored over the alternative which proposes a three-coordinate intermediate [9]. The compounds $PtMe_2(L-L)$ (L-L = bipy, phen) react with methyltin- or aryltin-halides SnR_nCl_{4-n} (R = Me, Ph; n = 0-3) and $PbPh_2Cl_2$ or $PbPh_3Cl$, to give oxidative addition into the Sn-Cl and Pb-Cl bonds. Quantitative yields of the compounds $PtMe_2Cl(L-L)(SnR_nCl_{3-n})$ and $PtMe_2Cl(L-L)(PbPh_mCl_{3-m})$ are obtained in close to quantitative yield [10]. Electronic and steric effects have been considered in a study of the rate of addition of MeI to $Pt(diaryl)_2(bipy)$ complexes [11]. For a series of substituted aryls, the second-order rate constants follow the series: R = Me > $4\text{-}MeOC_6H_4$ > $4\text{-}MeC_6H_4$ > $3\text{-}MeOC_6H_4$ > Ph > $4\text{-}FC_6H_4$ > $4\text{-}ClC_6H_4$ > $3FC_6H_4$. This order correlates with the energy of the metal-to-ligand charge-transfer transition in the electronic spectra of these platinum(II) complexes. This correlation is shown below. It has been shown that

$$\{NiX[(Ph_2PCH_2CH_2)_3N]\}BPh_4 + MeMgX \longrightarrow \{NiMe[(Ph_2PCH_2CH_2)_3N]\}BPh_4 + MgX_2$$

(6)



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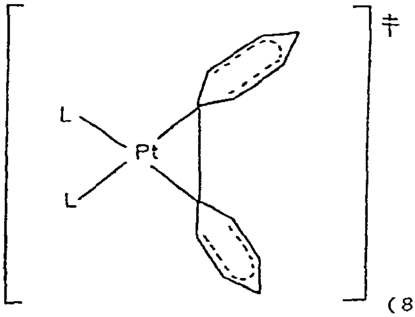
the product obtained by treating $PdMe_2L_2$ (L = PEt_3, PPh_2Me) with CO_2 is $PdMe(HOCO_2)L_2$, and not $PdMe(CO)_2L_2$ [12]. The yield of this bicarbonato product is less than 1% under anhydrous conditions. The structure of the triethylphosphine complex shows the bicarbonate to be a monodentate ligand, although it is likely that there is strong hydrogen bonding between molecules. A series of complexes $PtEt_2(L-L)$ ((L = dpe, dpp, dpb) have been prepared, and shown to selectively cleave one ethyl group with hydrogen chloride [13]. The change in ^1J (PPt) for $PtEt_2(L-L)$ follows the sequence dpp(1592Hz) < dpe(1602Hz) < PPh_2Me(1667Hz) < dpb(1677Hz) < PPh_3(1709Hz). The same sequence is found for the analogous dichloro compounds. A study of the symmetrization reactions of PtR_2L_2 with PtX_2L_2 to give $PtXRL_2$ has been made (R = Me, Ph, C≡CMe; L = PEt_3, PMe_3, $PPhMe_2$, $AsMe_3$; X = Cl, I, NCS, NO_2, NO_3). The dependence of rate on R and L in PtR_2L_2 follows the sequence R = Me > Ph > C≡CMe and L = PEt_3 > PMe_3 > $PPhMe_2$ > PPh_2Me [14]. These data correlate with basicity arguments. The rate data cover a wide range of reactivity. Interestingly the symmetrization reaction between <u>cis</u>-$PtMe_2(PPhMe_2)_2$ and <u>cis</u>-$PtCl_2(PPhMe_2)_2$ is catalyzed by $PtCl_2(\mu-Cl)_2(PPhMe_2)_2$. Complexes such as $PtMe_2(PPhMe_2)_2$ are readily oxidized by hexachloroiridate(IV) to give dimethylplatinum(IV) species; whereas the diethyl analogue $PtEt_2(PPhMe_2)_2$ gives EtCl and a monomethylplatinum(II) complex [15]. Two moles of hexachloroiridate(IV) are involved, and the rate-limiting step is electron transfer from dialkylplatinum(II) to hexachloroiridate(IV). The electrochemical oxidation of a nickel or a palladium anode in the presence of organic halides yields the unstable RMX species. These species can be stabilized by tertiary phosphines. The method can be used to prepare cyanide complexes of general formulae $RN{:}CN{\cdot}L_2$ (7) [16].

$$Ni + EtCN + 2PEt_3 \xrightarrow{[O]} EtNiCN{\cdot}2PEt_3$$

(7)

The thermal decomposition of complexes cis-PtR_2L_2 (R = Ph, p-tolyl; L_2 = $(PPh_3)_2$, $(P(p\text{-tolyl})_3)_2$, $(PPh_2Me)_2$, dpm, dpe, $Me_2PCH_2CH_2PMe_2$) in toluene solution shows that only complexes of monotertiary phosphines are labile at 60°. Reaction occurs by a primary concerted unimolecular reductive elimination of biaryl, and follows a first-order kinetic rate law. Concurrent secondary decomposition of PtL_2 generates both arene and biaryl as minor products. The addition of free tertiary phosphine accelerates primary decay. A transition state as shown in (8) is suggested [17]. A competition reaction has been carried out between electrophiles, HCl and $HgCl_2$, and complexes cis-$PtMe(p\text{-tolyl})(PPhMe_2)_2$ and $PtMe(p\text{-tolyl})(1,5\text{-COD})$. For the former complex Me-Pt cleavage occurs, but for the latter the preferential cleavage is at the Ph-Pt bond [18]. Several alkylpalladium and -platinum compounds of general formulae MR_2L_2 and $MRXL_2$ have been decomposed by UV irradiation. In chlorocarbon solvents the products are metal chloride and an organic material derived from the alkyl radical. CIDNP experiments on the UV irradiation of $PtMe_2(dpe)$



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$$PtMe_2L_2 \xrightarrow{h\nu} PtMeL_2 + Me^{\bullet}$$

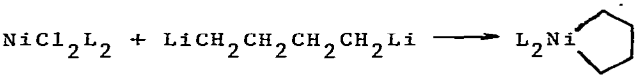
$$PtMeL_2 + CDCl_3 \longrightarrow PtClMe(CDCl_2)L_2$$

$$PtClMe(CDCl_2)L_2 \longrightarrow PtCl_2L_2 + CDClMe^{\bullet}$$

$$CDClMe^{\bullet} + CCl_3^{\bullet} \longrightarrow CCl_3CDClMe \text{ and } HCCl_3 + CDCl{=}CH_2$$

in $CDCl_3$ solution show the formation of radicals [19].

A series of nickelocyclopentanes (9) have been prepared from 1,4-dilithiobutane and the corresponding nickel halides [20]. The reaction is affected by added phosphine ligand, the data being accomodated in the following sequence. In further nickel work these authors have shown that the ratio of ethylene:cyclobutane is 9:1 on the decomposition of $(PPh_3)_3Ni(C_4H_8)$ at 9° C [21]. Other metallocyclic nickel complexes (10) have been obtained by treating Ni(1,5-COD)(bipy) with 3,3-dimethylcyclopropene. Complex (10) decomposes with C-C bond formation at 130° C or in the presence of oxygen. The structure of complex (10) has been solved and the molecule has an angle of 83.6°



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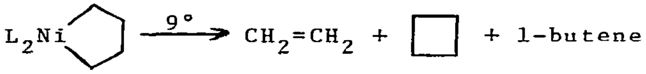
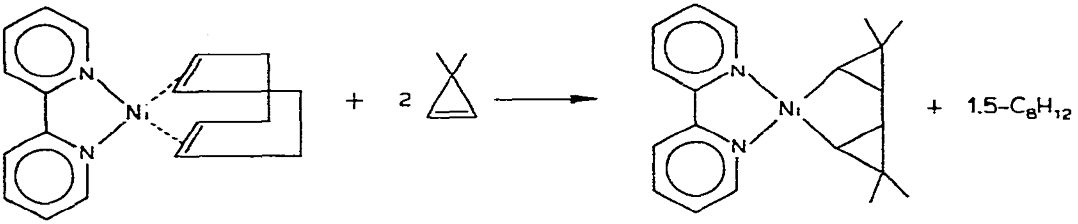


$(L = PPh_3,\ PCy_3,\ dpe)$

$$\begin{tikzcd} & LNi(C_4H_8) \arrow[r, shift left, "L"] \arrow[d] & L_2Ni(C_4H_8) \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & L_3Ni(C_4H_8) \arrow[l, shift left] \\ \text{Major product} & \text{1-butene} & \text{cyclobutane} & \text{ethylene} \end{tikzcd}$$



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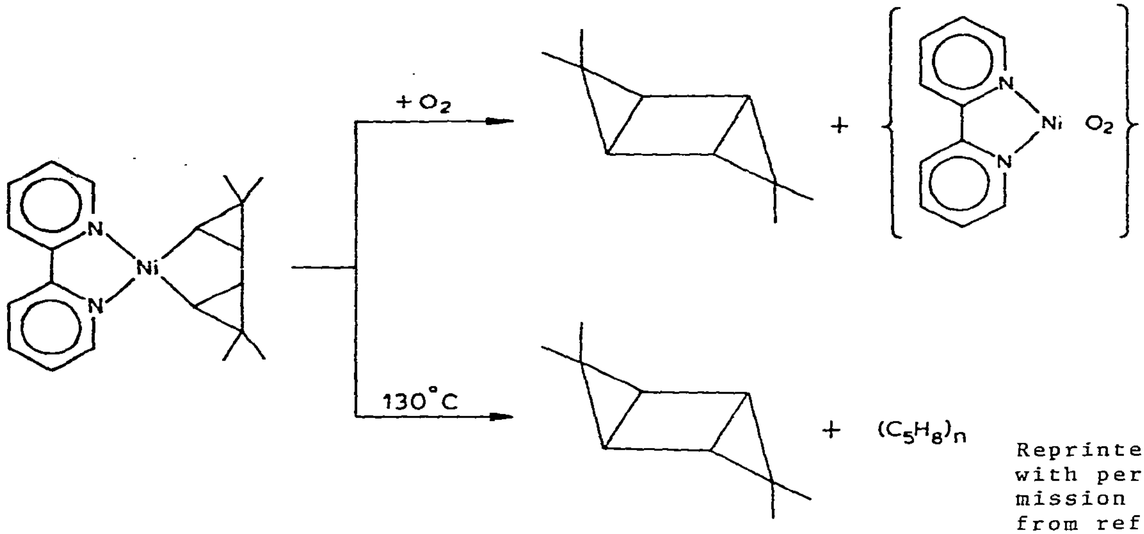
for C-Ni-C, with Ni-C distances of 1.904Å [22]. Complexes of platinum with spiroalkanes have been isolated. These compounds are formed by the addition of the C-C bond of the cyclopropane ring to platinum(II) to give the σ-bonded complex (11) [23]. The specifically deuterated cyclopropanes, trans-1-n-hexyl-cis-2,3-dideuterio cyclopropane and cis-1-n-hexyl-cis-2,3-dideuterio cyclopropane, have been reacted with $[PtCl_2(C_2H_4)]_2$ [24]. Analysis of the NMR spectra showed the



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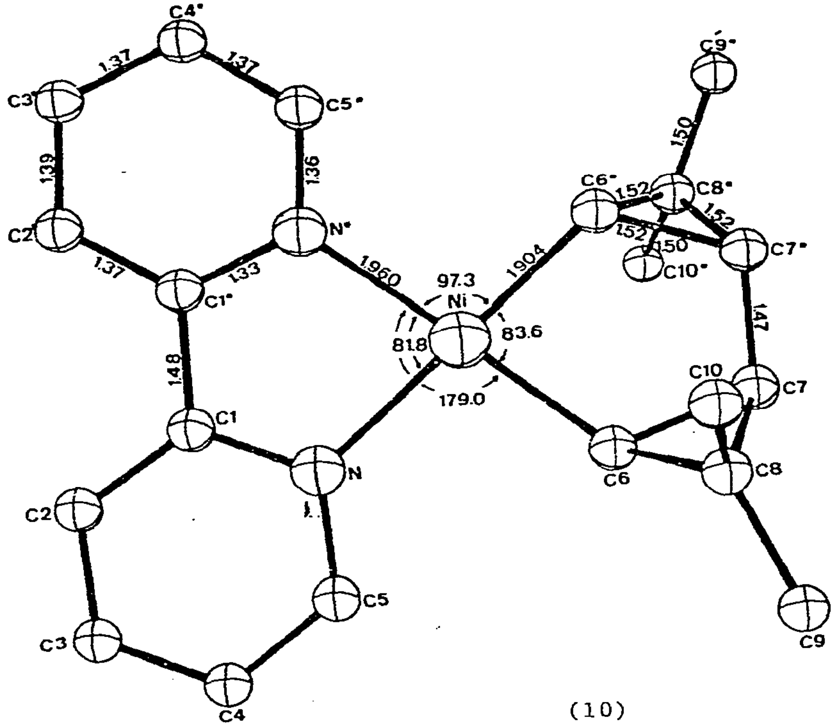
reaction to be stereospecific with retention of configuration at both reacting carbons. A concerted cycloaddition mechanism is suggested. The photolysis of the metallocyclopropane complexes



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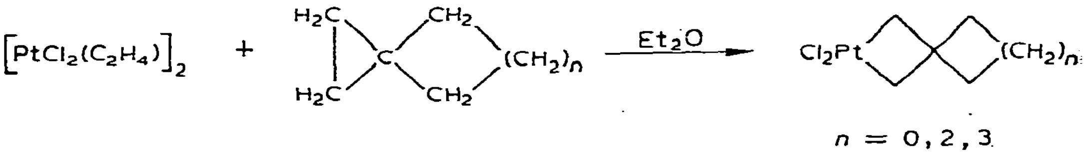

(11)

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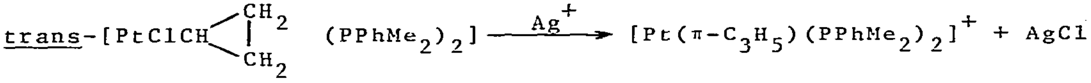
$PtX_2(C_3H_6)(L-L)$ (L-L = bipy, phen) at 25° C gives cyclopropane and $PtX_2(L-L)$. The first-order plot obtained has been used to suggest elimination of cyclopropane in a single step [25]. Complex (12), obtained from cis-$PtCl_2(PPhMe_2)_2$ and $Li[C_3H_5]$, undergoes rearrangement to a π-allyl platinum complex [26].



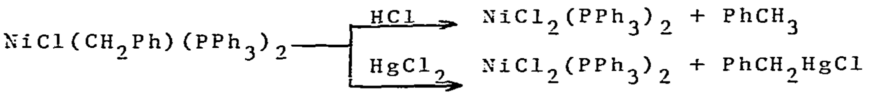
$$\text{trans-}[PtClCH(CH_2)_2(PPhMe_2)_2] \xrightarrow{Ag^+} [Pt(\pi\text{-}C_3H_5)(PPhMe_2)_2]^+ + AgCl$$

(12)

The oxidative addition of benzyl chloride or bromide to $Ni(PPh_3)_4$, followed by carbonylation and addition of methanol, yields methyl phenylacetate. Use of (R)-α-D benzyl chloride results in formation of racemic ester, and it is considered likely that the racemization occurs in the oxidative addition step [27]. The oxidative addition of benzyl chloride to $Ni(C_2H_4)(PPh_3)_2$ at -20° gives $NiCl(CH_2Ph)(PPh_3)_2$ (13) [28]. In benzene solution an equilibrium exists between $NiCl(\sigma\text{-}CH_2Ph)(PPh_3)_2$ and the blue violet $NiCl(\pi\text{-}CH_2Ph)(PPh_3)_2$. The benzyl ligand can be displaced by reaction with HCl or $HgCl_2$ to give toluene and $PhCH_2HgCl$, respectively. A complex $Ni(CH_2Ph)(acac)PPh_3$ has been prepared from $Ni(acac)_2$, tribenzylaluminum and triphenylphosphine [29]. Similar complexes with $P(CH_2Ph)_3$ and PCy_3 have also been

$$Ni(C_2H_4)(PPh_3)_2 + PhCH_2Cl \longrightarrow NiCl(CH_2Ph)(PPh_3)_2 + C_2H_4$$

(13)



$$NiCl(CH_2Ph)(PPh_3)_2 \begin{cases} \xrightarrow{HCl} NiCl_2(PPh_3)_2 + PhCH_3 \\ \xrightarrow{HgCl_2} NiCl_2(PPh_3)_2 + PhCH_2HgCl \end{cases}$$

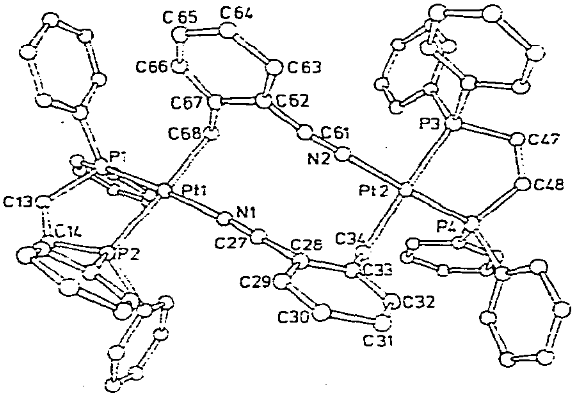
(13)

obtained in this manner. When $PdCl_2$(1,5-COD) is treated with lithiated phenyl methyl sulfone a crystalline complex $PdCl(CH_2SO_2Ph)$(1,5-COD) (14) is formed [30]. The Pd-CH_2 bond distance is 2.042(5)Å.

$$PdCl_2(1,5\text{-}COD) + PhSO_2CH_2Li \longrightarrow PdCl(CH_2SO_2Ph)(1,5\text{-}COD) + LiCl$$

(14)

The benzyl bond has been cleaved by peroxy acid [31]. With *m*-chloroperbenzoic acid, the compound $PtCl(PhCHD)(PPh_3)_2$ yields [^{2}H]benzyl *m*-chlorobenzoate and [^{2}H]benzyl alcohol, with retention of stereochemistry at carbon. A single crystal structure of the compound $[Pt(\underline{o}\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ (15) shows it to be a dimer with linear Pt-N≡C bonds. The CN group remains σ-coordinated to the metal in solution and is very prone to nucleophilic attack by water, alcohols, and amines, giving imide, iminoether, and amidine complexes, respectively [32]. The oxidative addition of benzyl, *o*-, *m*-, and *p*-cyanobenzyl chlorides to $Pd(PPh_3)_4$, yields *trans*-$PdCl(CH_2C_6H_4Y)(PPh_3)_2$ (Y = H, CN) (16). In solution these complexes are in equilibrium with the dimers $[PdCl(CH_2C_6H_4Y)(PPh_3)]_2$ (17), which can be quantitatively produced by oxidation of the free triphenylphosphine with H_2O_2 [33].



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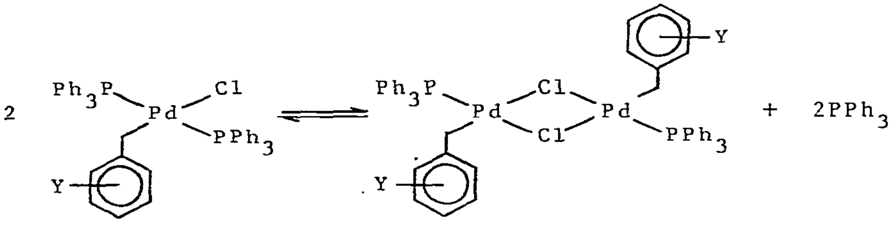
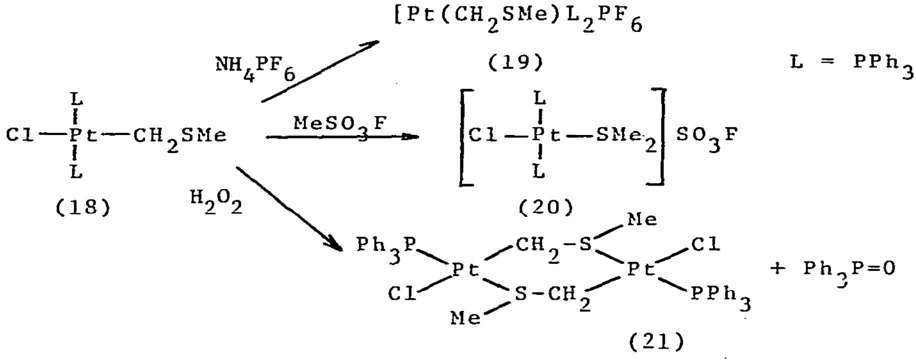


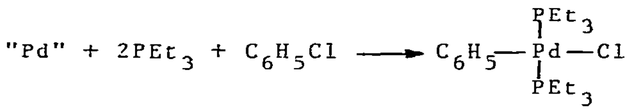
(16) (17)

Oxidative addition of $ClCH_2SMe$ to PtL_4 gives trans-$PtCl(CH_2SMe)L_2$ (L = PPh_3, PPh_2Me) (18) which can be converted to the ionic compound $[Pt(CH_2SMe)L_2]X$ (19). Treatment with $MeSO_3F$ yields a new type of dimethylsulfonium methylide platinum complex, trans-$[PtCl(CH_2SMe_2)L_2]SO_3F$, (20), and reaction with H_2O_2 yields $[PtCl(\mu\text{-}CH_2SMe)PPh_3]_2$ (21) [34]. Aryl, vinyl, and acyl halides react with



L = PPh_3, PPh_2Me

$Ni(C_2H_4)(PEt_3)_2$, $Ni(1,5\text{-}COD)(PEt_3)_2$, and $Ni(PEt_3)_4$ to give complexes trans-$NiX(R)(PEt_3)_2$ [35]. The nickel-aryl complexes can be carbonylated to give aroyl derivatives. A similar type of oxidative addition reaction has been carried out with nickel, palladium, and platinum metal powders [36]. Reduction of $PdCl_2$ with potassium, in the presence of triethylphosphine, in THF as solvent, yields a highly reactive black palladium slurry which will oxidatively add C_6F_5Br or C_6H_5I. Even chlorobenzene gives a 54% yield of $PdCl(C_6H_5)(PEt_3)_2$ (22). The compound $Ni(PPh_3)_4$ reacts with a chloro- or bromo-pyridine



$$\text{"Pd"} + 2PEt_3 + C_6H_5Cl \longrightarrow C_6H_5\text{—}\underset{PEt_3}{\overset{PEt_3}{Pd}}\text{—}Cl$$

(22)

to give a dimeric complex $[NiX(\sigma\text{-pyridyl})PPh_3]_2$. The bridging ligands can be readily substituted by other halide or pseudohalide ions [37]. Phase-transfer catalysis using crown ethers has been used to prepare complexes Pt(OH)Ph(dpe) and $[Pt(OH)(p\text{-}MeC_6H_4)(PPhEt_2)]_2$ from chlorocomplexes and aqueous KOH [38]. The Reformatsky reagent $BrZnCH_2CO_2Et$ reacts with aryl complexes of nickel and palladium to give good yields of aryl acetic acid esters. The reaction can be catalyzed by use of zerovalent complexes of these metals [39].

The reactions of $(C_6F_5)_2TlX$ with the nickel(I) complexes $NiXL_3$ (X = Cl, Br, I; L = PPh_3, $AsPh_3$) lead to the formation of the nickel(II) complexes $NiX(C_6F_5)L_2$ (23) [40]. The same products can be obtained from the complexes $NiX(CO)_2(PPh_3)_2$. Metathetical

$$2\ NiXL_3 + Tl(C_6F_5)_2Br \longrightarrow TlBr + 2\ NiX(C_6F_5)L_2 + 2\ L$$

(23)

reactions of $NiBr(C_6F_5)(PPh_3)_2$ with salts NaI, $NaNO_2$, $NaNO_3$, KCN, KSCN, $AgClO_4$ give the complexes $NiX(C_6F_5)(PPh_3)_2$ [41]. The perchlorate is readily displaced with neutral ligands to give cationic complexes. Dimeric complexes $[PtR'_2(SR_2)]_2$ (R' = Ph, p-tolyl) have been prepared from cis-$PtCl_2(SR_2)_2$ (R = Et, Pr) using excess LiR'. These dimeric complexes can be cleaved by neutral ligands such as SR_2, PPh_3, Me_3CNC, py, CO [42]. Variable-temperature ^1H and ^{19}F NMR spectroscopy on cis-cis-trans-$PtX_2(C_6F_5)_2(PEt_3)_2$, and mer-trans-, and mer-cis-$PtX_3(C_6F_5)(PEt_3)_2$ (X = Cl, Br), shows that at low temperatures the rotation of the phosphine ligands is prevented by steric interaction with cis-pentafluorophenyl groups [43]. Upon addition of excess of the Grignard compound $MgBr(C_6F_5)$ to a suspension of $[PdCl_2L]$ (L = PPh_3, PEt_3, PBu_3) the perfluoroaryl compound $[PdBr(C_6F_5)L]_2$ (24) is formed [44]. Mononuclear complexes have been formed by cleavage of the bridge with neutral ligands. Organometallic complexes of palladium(IV) (25)

$$2PdCl_2L + 2MgBr(C_6F_5) \longrightarrow [PdBr(C_6F_5)L]_2 + 2MgCl_2$$

(24)

have been obtained by the oxidative addition of chlorine to the palladium(II) compound $PdCl(C_6F_5)(L\text{-}L)$ (L-L = bipy, phen, N,N,N',N'-tetramethylethylenediamine) [45]. New complexes $NiCl(2,3,4,5\text{-}C_6HCl_4)L_2$, $NiCl(2,3,4,6\text{-}C_6HCl_4)L_2$, $NiCl(2,3,5,6\text{-}C_6HCl_4)L_2$, $NiCl(2,3,6\text{-}C_6H_2Cl_3)L_2$, and $NiCl(2,4,6\text{-}C_6H_2Cl_3)L_2$ (L = $2PPh_3$ or dpe) have been prepared by the reaction of the respective Grignard reagent with $NiCl_2L_2$ [46]. This author has also prepared the first pentachlorophenylplatinum(II) complexes of formula cis-$PtX(C_6Cl_5)(PEt_3)_2$ (X = Cl, Br, I, N_3, CN, NCS, OAc, NO_3, NCO, and NO_2) (26) and trans-$PtX(C_6Cl_5)(PEt_3)_2$ (X = Cl, Br, I, NCS) (27). The former compounds are obtained by the Grignard route, and the trans isomers result

$$PdCl(C_6F_5)(L\text{-}L) + Cl_2 \longrightarrow PdCl_3(C_6F_5)(L\text{-}L)$$

(25)

from vacuum sublimation of the cis isomer at high temperatures [47] The complex $NiCl(C_6Cl_5)(PPh_3)_2$, activated with silver perchlorate,

$$\underline{cis}\text{-}PtCl_2(PEt_3)_2 + C_6Cl_5MgCl \longrightarrow \underline{cis}\text{-}PtCl(C_6Cl_5)(PEt_3)_2 \xrightarrow{\Delta} \underline{trans}\text{-}PtCl(C_6Cl_5)(PEt_3)_2$$

(26) (27)

catalyzes ethylene dimerization in bromobenzene solvent. The catalytic activity is further enhanced by the addition of triphenylphosphine [48]. A series of complexes trans-$Ni(R)(C_6Cl_5)(PPhMe_2)$ (R = aryl) have been prepared. The stability of these complexes to decomposition is discussed, and it is noted that reaction of the compounds with CO leads to the formation of $R(C_6Cl_5)CO$ [49]. The compounds $Pd(C_6Cl_5)_2L_2$ (27) (L = N, As, S ligand; L ≠ phosphine) have been prepared by the reaction of $PdCl_2L_2$ with LiC_6Cl_5 [50]. The phosphine complexes (28) can be subsequently prepared by displacement of the neutral ligands L with a tertiary phosphine ligand. A series of stable complexes of type $[M(C_6F_5)_4]^{2-}$ (M = Ni, Pd) (29),

$$\begin{tikzcd} \underline{trans}\text{-}PdCl_2L_2 + 2LiC_6Cl_5 \arrow[r] & \underline{trans}\text{-}Pd(C_6Cl_5)_2L_2 + 2LiCl \arrow[d, "L'"] \\ & \underline{trans}\text{-}Pd(C_6Cl_5)_2L' + 2L \end{tikzcd}$$

(27)

L' = phosphine ligand

(28)

$[M(C_6Cl_5)_4]^{2-}$ (M = Ni) (29), and $[M(C_6F_5)_3(\text{tetrahydrothiophene})]^-$ have been prepared by the lithium method from the $[MCl_4]^{2-}$ (M = Ni) ion, or from $MCl_2(\text{tetrahydrothiophene})_2$ (M = Pd, Pt) complexes [51].

$$[\underline{n}\text{-}Bu_4N]_2[MCl_4] + 4C_6X_5Li \longrightarrow [\underline{n}\text{-}Bu_4N][M(C_6X_5)_4] + 4LiCl$$

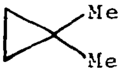
(29)

Generalized valence bond and configuration interaction calculations have been carried out for $NiCH_2$ and $NiCH_3$ [52]. In both cases the lower states have the character of $Ni(4s^13d^9)$ with the Ni 4s orbital bonding to the singly occupied Cσ orbital. Optimization of the geometries lead to values of 1.78Å for NiC in $NiCH_2$, and 1.87Å for NiC in $NiCH_3$. The calculated bond energies are $D(Ni\text{-}CH_3)$ =

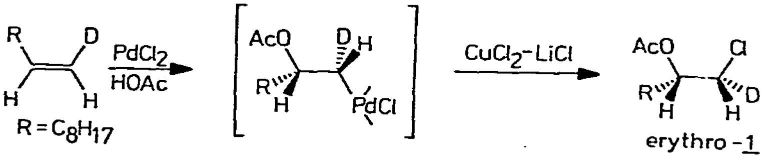
60 kcal, and D(Ni-CH_2) = 65 kcal, with a weak π bond in the latter case.

Palladium atoms have been co-condensed from the vapor phase with a series of alkyl halides to give oxidative addition products [53]. Trapping experiments, free-radical savenging experiments, and the distribution of decomposition products, suggest that metal atom C-X bond insertion occurs directly via a caged radical pair. An example

$$Me_3C{-}CH_2Br + Pd \xrightarrow{25°\ C} CH_4\ (16\%) + Me_3CH\ (3\%) + Me_4C\ (4\%)$$

$+ Me_2C{=}CH_2\ (51\%)\ +$  $(2\%) + PdBr_2\ (30\%)$

of such an experiment is shown above. In other work on the cleavage of Pd-C bonds, it has been shown that acetoxychlorination of Z-1-deuterio-1-decene occurs with inversion at the position where chloride replaces palladium. The oxidative cleavage of the Pd-C bond is effected with cupric chloride [54]. Methanol and stabilized enolates add to C-4 of homoallylic amines and sulfides in the presence of



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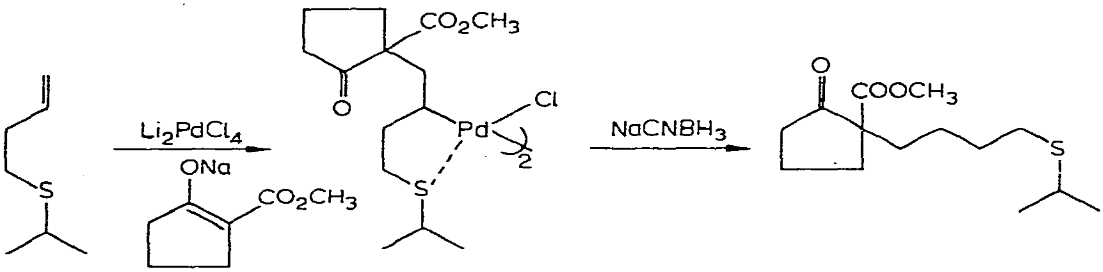
Li_2PdCl_4 to give stable chelated palladium complexes (30) in high yield. These complexes can be reduced with $NaCNBH_3$ to give ω-functionalized amines and sulfides [55]. The ^1H NMR spectra of the



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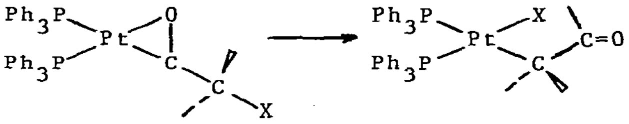
stable alkoxypalladation adducts of ethylene and cis-dideuterioethylene provide evidence for stereospecific trans alkoxypalladation of acyclic olefins [56]. The η-bonded ketone complex $Pt(\eta\text{-}CF_2ClCOCF_2X)(PPh_3)_2$ (X = F, Cl) (31) has been prepared from the reaction of $Pt(PPh_3)_4$ with $CF_2ClCOCF_2X$ [57]. These complexes isomerize in solution to cis-$PtCl(CF_2COCF_2X)(PPh_3)_2$ (32). The kinetics of this isomerization is reported. The structure of chloro(3-diethylaminopropionyl)(diethylamine)palladium(II) (33) shows bond lengths of 1.95(1)Å for Pd-C(acyl) [58]. Reactions with $AgBF_4$, Nacp, MeNC, and PPh_3 are also reported and discussed.



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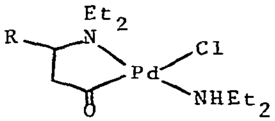


(33)

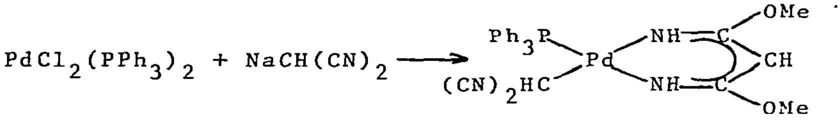
The addition of cyanogen to complexes of nickel(0) has been used to prepare dicyano nickel(II) complexes. For a broad range of phosphites (L), the 5-coordinate dicyano complexes $Ni(CN)_2L_3$ (34) have been isolated and the ^{31}P NMR spectra reported [59]. The complex Ni(CO)dpb undergoes a two-stage reaction with cyanogen. Initially

$$NiL_4 + (CN)_2 \longrightarrow Ni(CN)_2L_3 + L$$

(34)

almost equivalent amounts of $[Ni(CN)_2dpb]_2$ and $Ni(CO)_2dpb$ are formed, whereas in the second stage quantitative conversion of $Ni(CO)_2dpb$ into $[Ni(CN)_2dpb]_2$ occurs [60]. The first stage has been studied kinetically, and a proposed mechanism is presented. Cyclic voltammetry and controlled potential electrolysis have been used to investigate the redox reactions of trans-$Ni(CN)_2(PPhEt_2)_2$. In the first and the second process, the charge transfer step leads to unstable Ni(I) and Ni(0) complexes, both decaying in a short time to a dimeric nickel(I) complex. In a third process, the dimeric nickel(I) complex is reduced to a nickel(0) compound [61].

An unusual organopalladium complex (35) has been obtained by treating a methanol suspension of $PdCl_2(PPh_3)_2$ with sodium dicyanomethanide [62]. The complex (35) is considered from analytical and spectroscopic data to contain both an imino ether chelate and a $-CH(CN)_2$ ligand. In a study of the reaction of Pd(β-diketone)$_2$ with amines, it has been found that in the presence of excess amine the C-bonded ligand can be expelled from coordination [63]. Treating Na_2PdCl_4 with ethyl acetoacetate in aqueous alkali gives an intermediate (36) which converts to the O-bonded chelate (37) in dichloromethane solvent but which, in the presence of nitrogen bases, gives a C-bonded complex (38). This complex is in equilibrium with the C-bonded O-chelate complex (39) [64].



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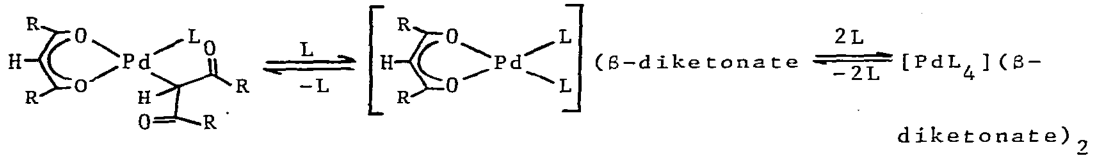
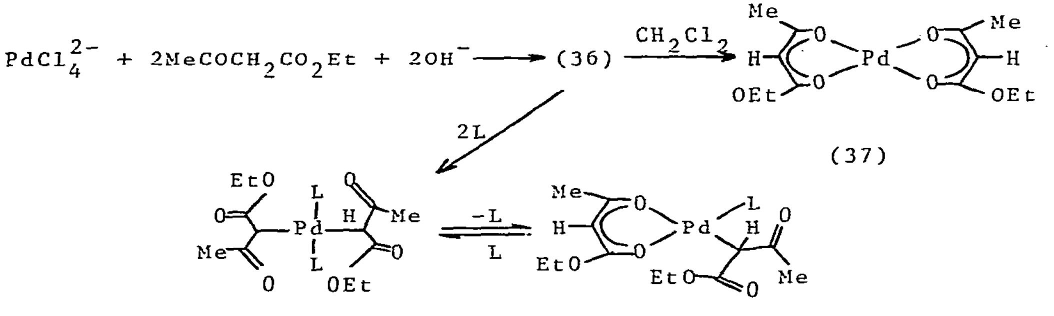


(L = amine)



(37)

(38) (39)

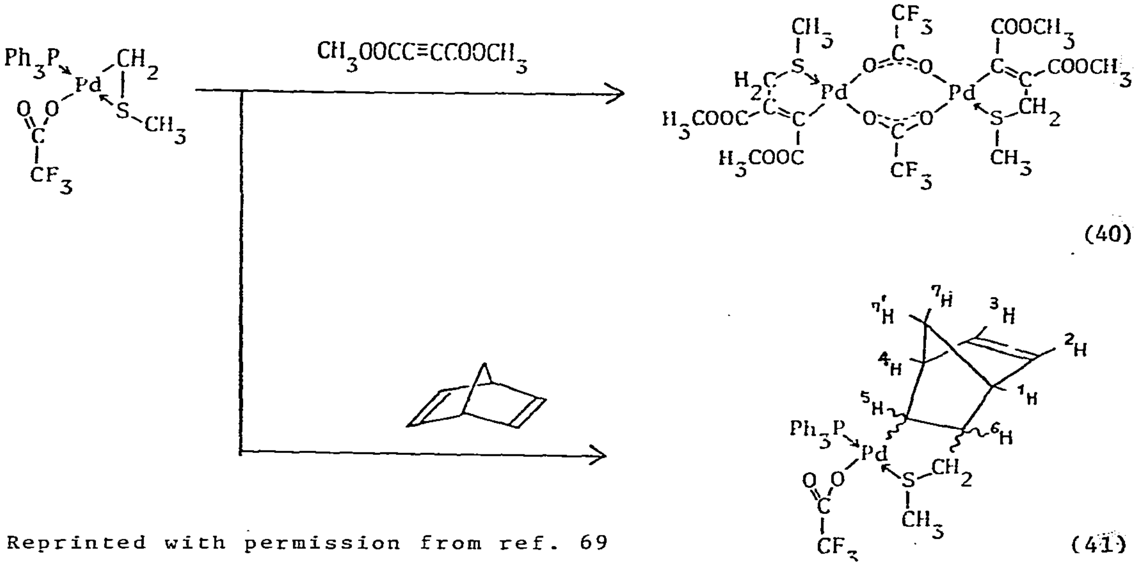
II. Metal complexes formed by insertion and related reactions

The reaction of trans-$[PtH(PEt_3)_2(acetone)]^+$, and trans-$[PtH(PEt_3)_2(CO)]^+$, with a range of acetylenes has been reported

[65]. For the acetone complex the pathway is considered to involve displacement of the acetone by the alkyne, followed by isomerization and insertion, and then re-combination with a ligand in the vacant coordination site thus created. For the carbonyl complex two pathways are involved. For strongly activated acetylenes (e.g. $(CF_3)_2C_2$) reversible loss of CO occurs, but with other acetylenes a 5-coordinate intermediate is involved. For the insertion of acetylenes $R_1C{\equiv}CR_2$

$$\begin{tikzcd}
\underline{trans}\text{-}[PtH(PEt_3)_2(acetone)]^+ \arrow[r, shift left, "R_2C_2"] & \underline{trans}\text{-}[PtH(PEt_3)_2(R_2C_2)]^+ \arrow[l, shift left, "acetone"] \arrow[d, shift left] \\
 & \underline{cis}\text{-}[PtH(PEt_3)_2(R_2C_2)]^+ \arrow[u, shift left] \arrow[d, shift left] \\
{[Pt(CR{=}CHR)(PEt_3)_2(acetone)]^+} & {[Pt(CR{=}CHR)(PEt_3)_2]^+} \arrow[u, shift left] \arrow[l, "acetone"']
\end{tikzcd}$$

into the Pt-H bond of trans-$PtHXL_2$ (X = NO_3, Cl; L = PEt_3, PCy_3) the alkenyl groups have a cis geometry. A four-centered transition state is proposed, and the disposition of the acetylene relative to the Pt-H bond is dependent on the Pt-H bond polarity [66]. In a subsequent paper these authors consider the insertion reaction in benzene as solvent which is considerably slower, and which gives some product with a trans geometry about both the metal center and the double bond. This reaction is accelerated by free-radical initiators, and gives a much higher fraction of trans-alkenyl product under these conditions [67]. The effect of increased pressure on the insertion of acetylenes into the Pt-H bond shows an acceleration of the reaction



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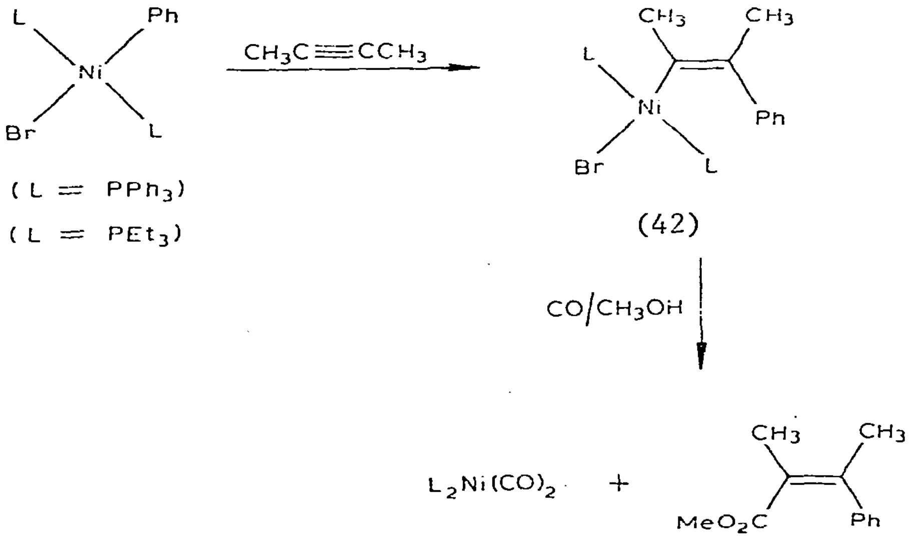
(41)

at high pressures. The effect is more enhanced in systems where it is considered likely that an ionic transition state is involved in the reaction pathway [68]. Both dimethyl acetylenedicarboxylate and 2,5-norbornadiene will insert into the Pd-C bond of the complex $Pd(CH_2SMe)(OCOCF_3)(PPh_3)_2$. The products (40) and (41) have been isolated and characterized [69]. 2-Butyne has been found to react stereospecifically with $NiBr(Ph)(PPh_3)_2$ in MeOH to give the vinyl complex $NiBr[$*cis*$-C(Me)=C(Me)Ph](PPh_3)_2$ (42) via insertion into the Ni-Ph bond. The complex (42) can be carbonylated to give *cis*-α,β-dimethylcinnamate (43) [70]. An intramolecular pathway has been suggested for the isomerization of the alkene complex $Pt(C_2F_3Br)(AsPh_3)_2$ (44) into the vinyl complex $PtBr(CF=CF_2)(AsPh_3)_2$ (45) [71].



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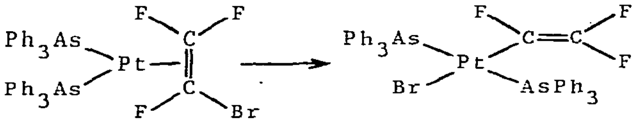
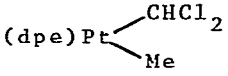


(44)

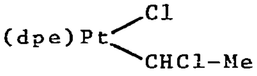
(45)

The reaction rate has been found to be little affected by change of solvent. Compounds of type M(R)(R')dpe (46) (R = alkyl, R' = dichloro- or trichloromethyl group which can serve as a carbene precursor) show an intramolecular rearrangement whereby the carbene moiety is inserted into the Pt–C or Pd–C bond to give the halo-ethyl complex (47) [72].



$(dpe)Pt(CHCl_2)(Me)$

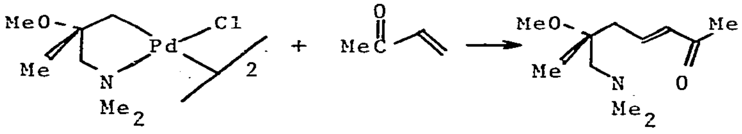
(46)



$(dpe)Pt(Cl)(CHCl{-}Me)$

(47)

Treatment of di-μ-chlorobis(2-methoxy-2-methyl-3-N,N-dimethylamino-propyl)dipalladium (48) with methyl vinyl ketone gives a compound (49) derived from olefin insertion into the Pd–C σ bond [73]. Other

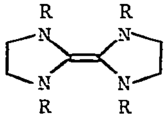


(48) (49)

examples of this type of reaction are given in the article.

III. Metal carbenes and ylides

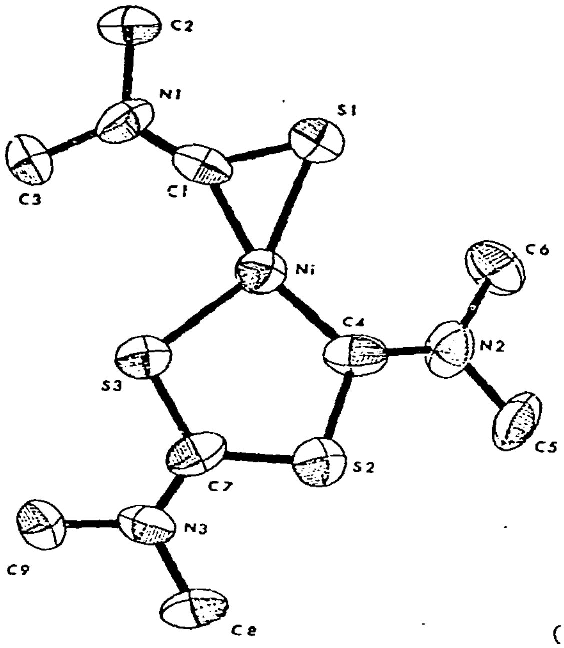
A series of carbene nickel complexes have been obtained from electron-rich olefins (50) [74]. Designating this ligand $(L^R)_2$, the series of complexes $Ni(CO)_3L^R$, $Ni(CO)_2L^R(PCy_3)$, trans-$NiCl_2(L^R)_2$,



(L^R_2: R = Me, Et)

(50)

cis-$NiCl_2(L^R)_2$, $Ni(CO)_2(L^R)_2$, $NiI_2(L^R)_2$, $Ni(L^R)_2(NO_3)_2$, $NiIL^R(PPh_3)$, $Ni(CO)_2L^R(PPh_3)$, and $[Ni_2(\mu\text{-}CO)(\eta\text{-}cp)_2(\mu\text{-}L^R)]$ have been isolated. Treating $Ni(CO)_4$ or $Nicp_2$ with dimethyl thiocarbamoyl chloride, followed by metathesis with $NaBPh_4$, gives the carbene complex $[Me_2NCSNiC(NMe_2)SC(NMe_2)S]BPh_4$ (51) [75]. The Ni–C distances are 1.854(11)Å and 1.909(10)Å for the bonds to the thiocarboxamido and carbene ligands, respectively. Little π-interaction between the nickel atom and the carbenoid carbon atoms is considered likely. In continuing work on the chemistry of σ-bonded α-diimino groups,



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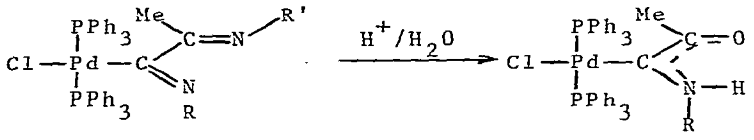
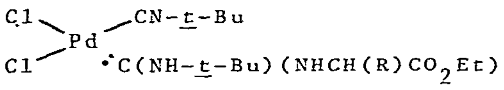
(51)

it has been reported that treatment with aqueous acid yields acetylimino complexes (52) [76]. Imidazolanes, dihydrooxadiazinones, and



(52)

tetrahydrotriazinones, have been prepared by the $PdCl_2$ catalyzed reaction of isonitriles with α-amino acid esters, with α-hydroxy acid hydrazides, and with α-amino acid hydrazides, respectively. The intermediate diaminocarbene palladium(II) complexes (53) have been isolated [77]. A kinetic study has been made of the reaction of



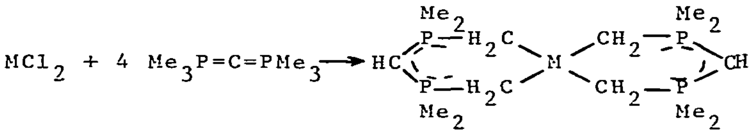
$$Cl_2Pd(CN\text{-}\underline{t}\text{-}Bu)(\dot{C}(NH\text{-}\underline{t}\text{-}Bu)(NHCH(R)CO_2Et))$$

(53)

aromatic amines with the complexes <u>cis</u>-$PdCl_2(CNAr)_2$ (Ar = Ph, <u>p</u>-tolyl, <u>o</u>,<u>o</u>'-$Me_2C_6H_3$). Secondary amines give monocarbene complexes <u>cis</u>-[$PdCl_2${C(NHAr)NRAr'}CNAr] (R = Me, Et; Ar' = Ph, <u>p</u>-tolyl, <u>p</u>-anisyl), while unhindered primary anilines react further to give bis-carbene complexes $PdCl_2\{C(NHAr)NH\text{-}p\text{-}tol\}_2$ [78]. A stepwise mechanism is proposed which involves a direct nucleophilic attack of the entering amine on the isocyanide carbon, followed by proton transfer to the final mono- or bis-carbene complexes. Stable cationic alkyoxycarbene complexes *trans*-$[Pt(C{\equiv}CR)\{C(CH_2R)OR'\}L_2]PF_6$ and *trans*-$[PtCl\{C(CH_2R)OR'\}L_2]PF_6$ have been obtained by treating the platinum acetylide complexes, *trans*-$Pt(C{\equiv}CR)_2L_2$ and *trans*-$PtCl(C{\equiv}CR)L_2$, with acids HX and alcohols R'OH (R = H, Me, Ph; L = $PPhMe_2$, $AsMe_3$; R' = Me, Et, *n*-Pr, *i*-Pr) [79]. In the following paper evidence is presented supporting the intermediacy of a platinum-stabilized vinyl cation $Pt\text{-}\overset{+}{C}{=}CH_2$ [80]. Electrophilic attack at both sulfur atoms of the complex $Pt(\pi\text{-}CS_2)(PPh_3)_2$ by MeI or EtI results in the initial formation of a cationic carbene complex $[PtI\{C(SR)_2\}(PPh_3)_2]I$ (54) [81]. Under reflux conditions loss of PPh_3 occurs from this compound (54) to give a neutral carbene complex (55).

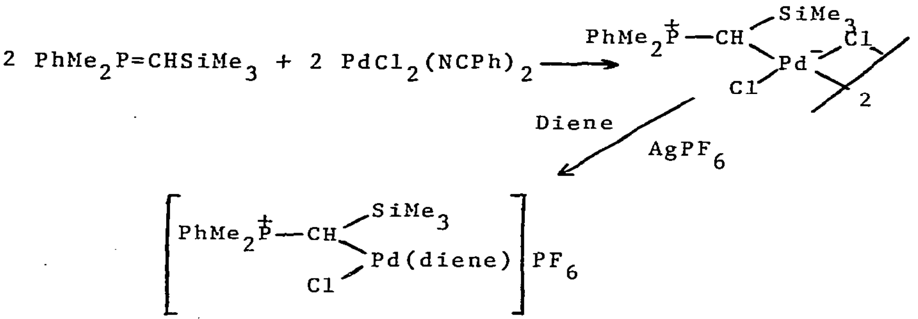
$$Pt(\pi\text{-}CS_2)(PPh_3)_2 + 2RI \longrightarrow \underset{(54)}{[PtI\{C(SR)_2\}(PPh_3)_2]I} \longrightarrow \underset{(55)}{PtI_2\{C(SR)_2\}PPh_3}$$

Among a series of ylide complexes, the reaction between MCl_2 (M = Ni, Pd, Pt) and $Me_3P{=}C{=}PMe_3$ is reported to give the ylide complexes $M[CH_2P(Me)_2CHP(Me_2)CH_2]_2$ (55) [82]. ^1H NMR data is reported



(55)

for the complexes. In the following paper similar complexes with Ni and Pt are reported from the ligand $[Me_3P{=}N{=}PMe_3]^+$, where now the ring CH is replaced by an N atom [83]. A dimeric η^1-ylide palladium complex $[\{PhMe_2\overset{+}{P}\text{-}CH(SiMe_3)\}Cl_2Pd^-]_2$ (56), prepared from $PdCl_2(NCPh)_2$ and $PhMe_2P{=}CHSiMe_3$, is converted to a new η^1-ylide cyclic diolefin complex $[\{PhMe_2\overset{+}{P}\text{-}CH(SiMe_3)\}Cl(diolefin)Pd]PF_6$ (57) on treatment with $AgPF_6$ in the presence of 1,5-COD or NBD [84]. A crystal structure of the previously reported ylide complex [(Benzoylmethylene)diphenyl-2-(diphenylphosphino)ethylphosphorane]dichloropalladium(II) shows a Pd-C distance to the ylide of 2.115(15)Å [85]. The trans influence of the ylide ligand is slightly less than that of the phosphine group. Complexes of Pd(II) and Pt(II) with the sulfur ylide $Me_2\overset{+}{S}(O)\overline{C}HCOPh$



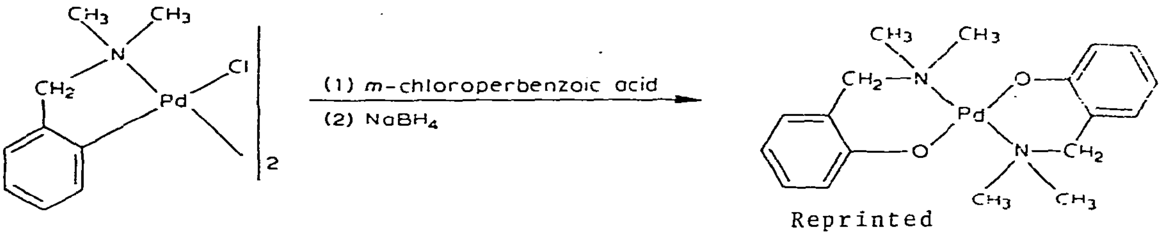
(56)

(57)

of formulae $[PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}SEt_2]$ and $PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}$ have been prepared [86]. Binding energies are given.

IV. Internal metalation reactions

A preliminary communication has described the formation of a salicylaldaminato palladium(II) complex (59) by treatment of di-μ-chlorobis[α-(dimethylamino)-2-tolyl)dipalladium (58) with *m*-chloroperbenzoic acid [87]. A further reaction of *ortho* palladated benzylic amines is their reaction with methyl vinyl ketone to give organic products arising from arylation of the olefin [88].



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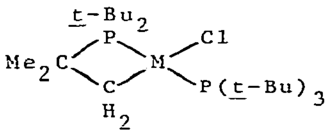
An interesting intramolecular metalation of tri-*t*-butylphosphine with platinum(II) and palladium(II) has been reported [89]. Thus treatment of the compound $PtCl_2$ with $P(t\text{-}Bu)_3$ results in the formation of $[P(t\text{-}Bu)_3H]_2PtCl_4$ and the internally metalated complex *trans*-$PtCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$ (60). Resolution of some racemic tertiary



(60)

phosphines have been achieved with chloro-bridged chiral palladium(II) complexes (61) and (62) [90]. The crystal structure and absolute configuration of [(S)-isopropyl-*t*-butylphenylphosphine][(R)-N,N-dimethyl-α-(2-naphthyl)ethylamine-3C,N]chloropalladium(II) (63) has been determined. The first examples of transition metal *o*-metalated complexes of phosphine imides have been reported [91]. These cyclometalated compounds have been obtained in good yield by treating triarylphosphine imides with tetrachloropalladate in methanol. Fused organometallic chelate rings are obtained in compound (65) by the reaction of hydrazoximes (64) with Li_2PdCl_4 [92]. Cyclopalladation of vinylic oximes occurs with the sterically rigid oximes of 1-benzalcyclohexanone and 1-acetylcyclohexene to give dimeric complexes

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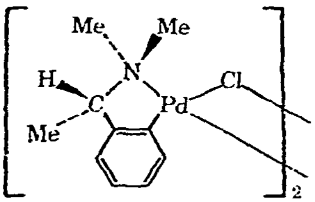

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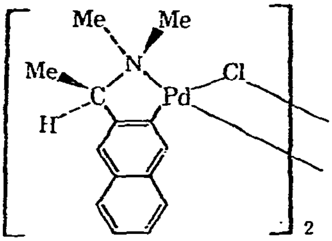

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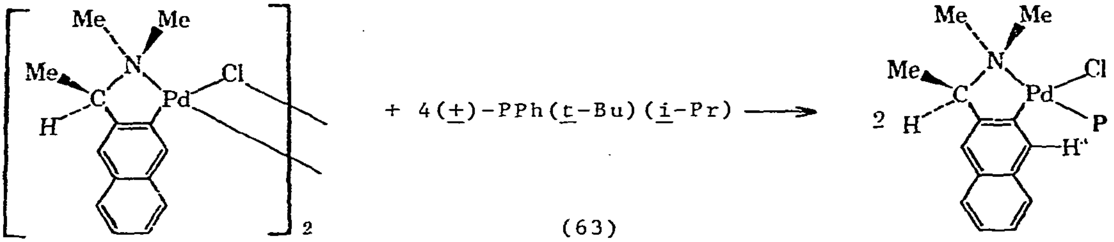

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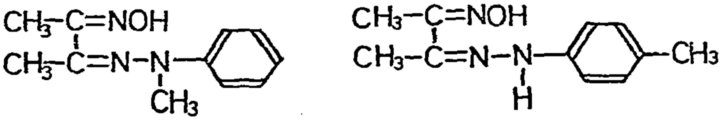

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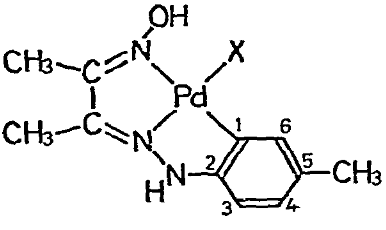

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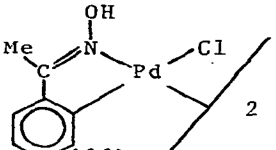
(65)

which retain the alkene double bond [93]. Complexes (66) and (67) have been prepared. The internal palladation of optically active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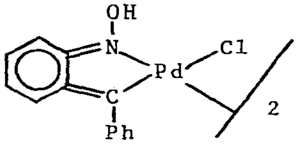

(67)

1-dimethylaminoethylferrocene proceeds with stereoselectivity 85/15 [94]. 2-Pyridylferrocene has been metalated with tetrachloropalladate [95]. A dimeric chloro bridged compound having both a Pd-C bond to ferrocene, and the nitrogen of the pyridine ring coordinated to Pd is formed, and subsequent reaction with Tl acac gives the monomeric acetylacetonate compound. The structure of the bimetallic complex containing a Pd-Co bond, tetracarbonylcobaltatopyridine {N(phenylamino)-α-methylbenzylidenimino-2-C,N}palladium(II), has a Pd-C bond length of 2.604(1)Å. The molecule contains a cyclopalladated ring system, with Pd-C and Pd-N(1) bond lengths of 1.998(8) and 2.101(5)Å, respectively. The palladium atom is bonded to a pyridine ring and to a $Co(CO)_4$ group trans to N(1). The complex is prepared by treating the corresponding chloro-complex with $NaCo(CO)_4$. A far infrared and Raman study of dimeric cyclopalladated complex has reported values of ν(Pd-Cl) and ν(Pd-Br) for a wide range of compounds [97].

V. Metal carbonyls and thiocarbonyls

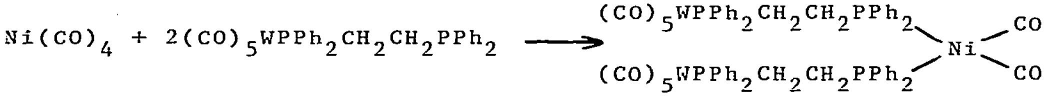
A few aspects of metal carbonyls have appeared in the 1977 literature which do not fall in the usual categories of chemical reactions and structure. There has been a further article on the occurrence of nickel carbonyl in cigar smoke [98]. The concentration of $Ni(CO)_4$ in nanomoles/liter of cigar smoke ranged from 65-159 over four brands. Of similar interest, a U.S. government recommendation has been made that the toxic level of $Ni(CO)_4$ should be kept at 1 p.p.b. [99]. A report appeared that $Ni(CO)_4$ may be the cause of Legionnaire's Disease [100], but it is since known that this is not the case.

Thermolysis to ∿300° C has been used to bond $Ni(CO)_n$ (n = 1-3) to cation exchange X-type zeolites, but the materials were inactive for catalytic hydrogen of benzene to cyclohexane until the carbonyl complexes were completely destroyed [101]. A series of complexes of general formula $Ni(CO)_x[(Ph_2N)_yPF_{3-y}]_{4-x}$ have been prepared by treating $Ni(CO)_4$ with diphenylaminofluorophosphines [102]. The CO ligand has been displaced from the complex Ni(CO)(dpb) (68) with tetracyanoethylene even in a 1:1 mole ratio [103]. With fumaronitrile a two-step reaction occurs to give $Ni(CO)_2(dpb)$ and Ni(dpb)(fumaronitrile). The complex reacts with phosphites, but not with nitriles or alkynes. The complex $W(CO)_5dpe$, having an

$$Ni(CO)(dpb)_2 + C_2(CN)_4 \longrightarrow Ni[C_2(CN)_4]dpb + CO + dpb$$

(68)

uncoordinated phosphine group, has been used as a ligand by treating it with nickel carbonyl. Two carbonyl groups are substituted and the product, $Ni(CO)_2[PPh_2CH_2CH_2PPh_2W(CO)_5]_2$ (69), formed [104]. A series of complexes have been isolated from the reaction of $Ni(CO)_4$

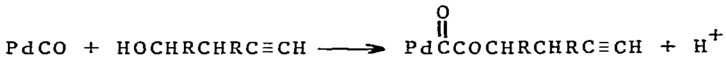


(69)

with P_4O_7. These compounds are formulated $[Ni(CO)_3](P_4O_7)$ and $[Ni(CO)_3]_2(P_4O_7)$ [105]. Structures are proposed based on analysis of the ^{31}P NMR spectra.

Simple approximate self-consistent field calculations for $Ni(CO)_4$ have been made with the Hartree-Fock-Slater model using numerical basis functions. The theoretical ionization energies are in good agreement with the experimental photoelectron spectra [106].

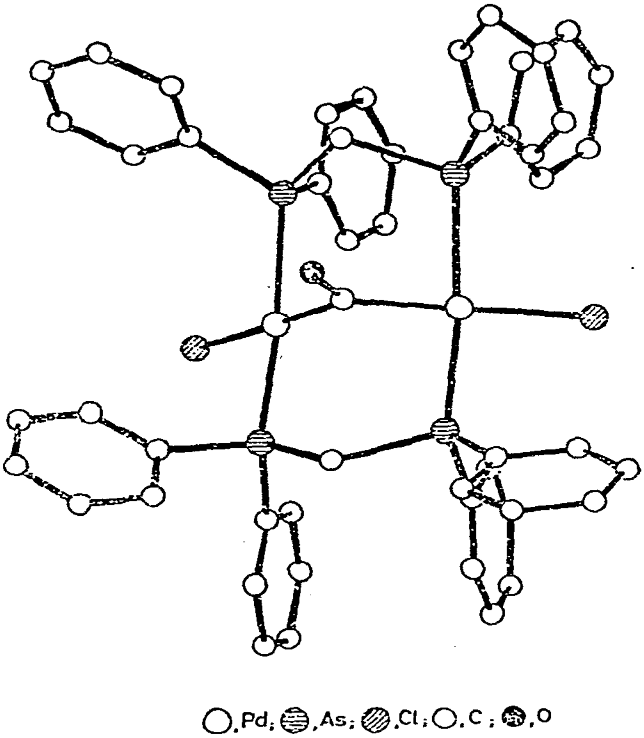
New carbonyls of palladium have been prepared by reacting CO with palladium acetate in glacial acetic acid solvent [107]. A crystalline diamagnetic complex $Pd_2(OAc)_3CO$ is formed. The compound was characterized by its infrared and photoelectron spectra. Mechanistic considerations of the palladium catalyzed synthesis of α-methylene lactones from carbon monoxide and acetylenic alcohols have been discussed [108]. These authors propose that nucleophilic attack by the alcohol end of a butynol occurs on a carbonyl ligand coordinated to palladium(II). This carboalkoxy species (70) can then add intramolecularly to the triple bond. Interaction of $Ph_2AsCH_2AsPh_2$ and



$$PdCO + HOCHRCHRC{\equiv}CH \longrightarrow Pd\overset{O}{\overset{\|}{C}}COCHRCHRC{\equiv}CH + H^+$$

(70)

dpm with the palladium(I) halogenocarbonyls PdX(CO) gives dimeric complexes. The arsine complex has been found to be a carbonyl complex $[PdClPh_2AsCH_2AsPh_2]_2CO$ with a bridging carbonyl and bridging diphenylarsinomethane ligands (71) [109]. The analogous carbonyl complex with dpm (72) has been obtained by carbonylation of $[PdXdpm]_2$. The reactions with isocyanides are also described [110]. Detailed infrared and Raman studies have been reported for compounds $[PtX_3(CO)]^-$ (X = Cl, Br, I), $[PdX_3(CO)]^-$, and cis-$PtX_2(CO)_2$ [111]. Stretching force constants have been evaluated. The results are discussed in conjunction with the ^1H NMR and the $^1H-\{^{31}P\}$ and $^1H-\{^{195}Pt\}$ INDOR spectra on the complexes. The alkoxycarbonyl complexes $[Pt(CO_2R)(CO)$



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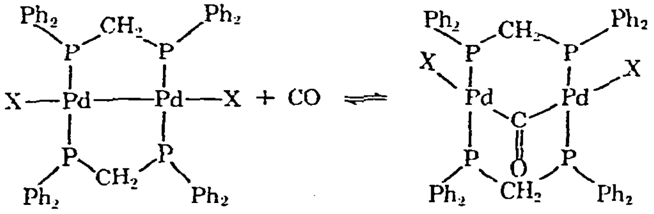

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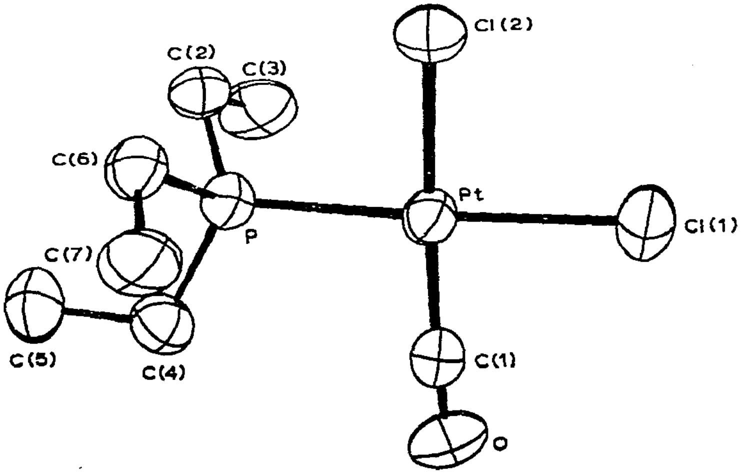
$(PPh_3)_2]BF_4$ react with alkynes $HC\equiv CH$ to give acetylides (73). When disubstituted acetylenes are reacted, the products are cationic β-methoxyvinyl (74) or β-hydroxyvinyl (75) complexes, respectively, depending on the nucleophile methanol or water [112].

$$\underline{trans}\text{-}[Pt(CO_2R)CO(PPh_3)_2]BF_4 + HC\equiv CR \rightarrow \underline{trans}\text{-}[Pt(C\equiv CR)CO(PPh_3)_2]BF_4 + CO \quad (73)$$

$$\xrightarrow{RC\equiv CR/MeOH} \underline{trans}\text{-}[Pt(CR{=}C(R)OMe)CO(PPh_3)_2]BF_4 \quad (74)$$

$$\xrightarrow{RC\equiv CR/OH} \underline{trans}\text{-}[Pt(CR{=}C(R)OH)CO(PPh_3)_2]BF_4 \quad (75)$$

An X-ray structure of cis-$PtCl_2(CO)PEt_3$ shows the compound to have a monomeric cis geometry (76) [113]. The pertinent distances are Pt-C = 1.855(14)Å, Pt-Cl(trans to C) = 2.296(4)Å, and Pt-Cl(trans to P) = 2.368(3)Å. An improved procedure to prepare the compound cis-$PtCl_2(CO)_2$ (77) consists of treating pre-dried hexachloroplatinic acid with CO in thionyl chloride. Carbonylation of either cis or trans-$PtCl_2(PPh_3)_2$ by CO can also be carried out with CO [114]. Fourier transform ^{195}Pt Nuclear Magnetic resonance has been used to probe the structures and stereochemical nonrigidity of large platinum carbonyl clusters [115]. The spectra for $[Pt_9(CO)_{18}]^{2-}$ have been interpreted on the basis of rotation of the outer Pt_3 triangles with



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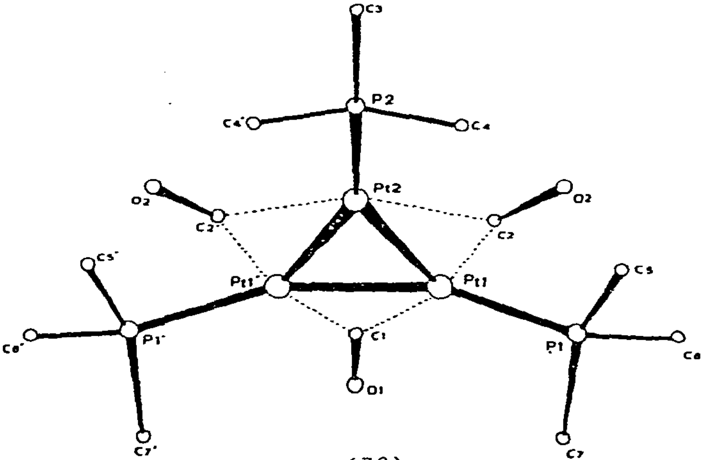
(76)

$$PtCl_n + \frac{n+2}{2}CO \xrightarrow{SOCl_2} PtCl_2(CO)_2 + \frac{n-2}{2}COCl_2 \qquad (77)$$

respect to the middle triangle. It has also been found that interexchange of Pt_3-triangles occurs in mixtures of $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ at 25° C. A crystal structure has been solved for the carbonyl platinum cluster compound $[Pt(CO)PCy_3]_3$ (78) [116].

$$[{}^{*}Pt_{12}(CO)_{24}]^{2-} + [Pt_9(CO)_{18}]^{2-} \rightleftharpoons [{}^{*}Pt_9(CO)_{18}]^{2-} + [Pt_9{}^{*}Pt_3(CO)_{24}]^{2-} \rightleftharpoons \text{etc.}$$

The Pt-Pt distances are in the range of 2.65Å, and the carbonyls are all bridging. A crystal structure of the complex $[PtCl(dpm)]_2CO$ has been published [117], which shows it to be similar to the palladium analog [110]. The Pt-Pt distance is 2.652(2)Å.



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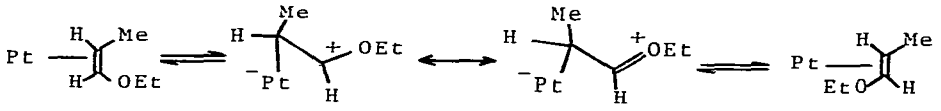
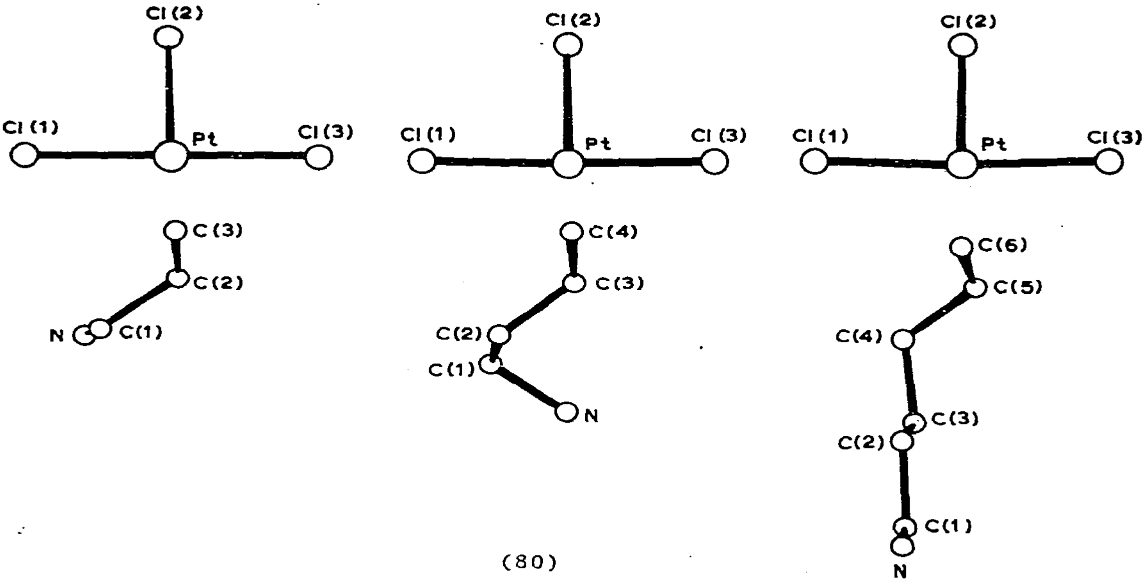
VI. Metal olefins and vinyls

The crystal structure of $K[PtCl_3(C_2H_4)]$ has been solved to a refinement of R = 0.026. The ethylene is in an upright position with an angle for olefinic-Pt-Cl of 94.7° [118]. The second-order rate constants have been measured for the reaction of ethylene with $[PtCl_4]^{2-}$, $[PtCl_3(OH_2)]^-$, and $PtCl_2(OH_2)_2$ in aqueous solution at 25° C [119]. The reaction is irreversible and the products are monoplatinum monoolefin complexes such as $[PtCl_3(C_2H_4)]^-$ and $PtCl_2(C_2H_4)(OH_2)$. Interestingly there are no large variations in rate between the three complexes, despite the large disparity in their charges. A convenient route to dimers $[PtCl_2(olefin)]_2$ (79) is to stir ether solutions of complexes trans-$PtCl_2$(olefin)L (L = neutral base, e.g. pyridine) with a large excess of cation exchange resin [120]. These complexes $[PtCl_2(C_2H_4)]_2$ and trans-$PtCl_2$(olefin)py have been used to catalyze

$$2\ \underline{trans}\text{-}PtCl_2(olefin)L + 2\overset{+}{H} \xrightarrow{Resin} [PtCl_2(olefin)]_2 + 2LH^+ \qquad (79)$$

alkoxide exchange of vinyl ethers RCH=CHOR' with alcohols [121]. When the reaction is carried out in acetonitrile solvent the vinyl ethers can be catalytically cis-trans isomerized with trans-$PtCl_2(C_2H_4)$py. The most likely pathway for this latter process is considered to pass through a trigonal carbon species by a π σ conversion of coordinated vinyl ether. The crystal structure of the olefin complexes trichloro(π-allylammonium)platinum(II), trichloro(π-but-3-enylammonium)platinum(II), and trichloro(π-hex-5-enylammonium)platinum(II) have been reported [122]. In all three complexes the platinum is four coordinate with the three chlorine atoms and the double bond of $CH_2{=}CH{-}(CH_2)_n{-}\overset{+}{N}H_3$ (n = 1, 2, 4) in the coordination sphere. The ordering of the zwitterion is shown below (80).





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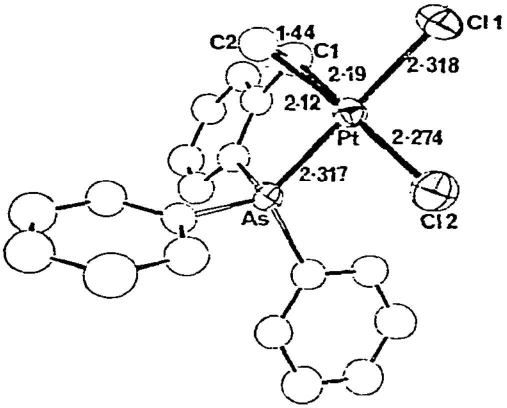
Two complexes of formulae trans-$PtCl_2L(CH_2CH_2L)$ (L = 4-Mepy, 3,5-Me_2py) (81) have been prepared by nucleophilic attack of free amine on the coordinated ethylene of trans-$PtCl_2(C_2H_4)L$ [123]. The reaction is restricted to the more basic and less hindered pyridines.

$$\text{trans-}PtCl_2(C_2H_4)L + L \longrightarrow \underset{(81)}{\text{trans-}PtCl_2L(CH_2CH_2L)}$$

Mechanisms and exchange processes are discussed. A series of complexes trans-$PtCl_2$(olefin)L (L = a nitrogen or oxygen bonded ligand, or Cl^-; and the olefin is cis-2-butene or a monosubstituted olefin) has been studied by infrared, Raman, UV and ^{13}C NMR spectroscopy [124]. The trans influence of L on the olefinic group follows the order O < Cl^- < N. This is observed in a decrease in $\nu(Pt-C_2)$, in the summed percentage lowering of the coupled $\nu(C=C)$, $\delta(CH)$ and $\delta(CH_2)$ vibrations, and in the increasing downfield $\delta\ {}^{13}C_{mean}$ shifts of the olefinic carbon atoms. The shift in $\delta\ {}^{13}C_{mean}$ after coordination is a measure of the variation of charge distribution between platinum and the olefin with respect to the ethylene compound. The value $^1J(^{195}Pt-^{13}C)$ is discussed in terms of σ-bond strength between Pt and the olefinic carbon atoms, and decreases in the order O < Cl^- < N. The crystal structure of the complex $PtCl_2$(o-vinylAsPh_2) (82) shows a square planar coordination geometry with the coordinated olefin making an angle of 83.6° with this plane [125]. The Pt-As bond length is 2.275Å.



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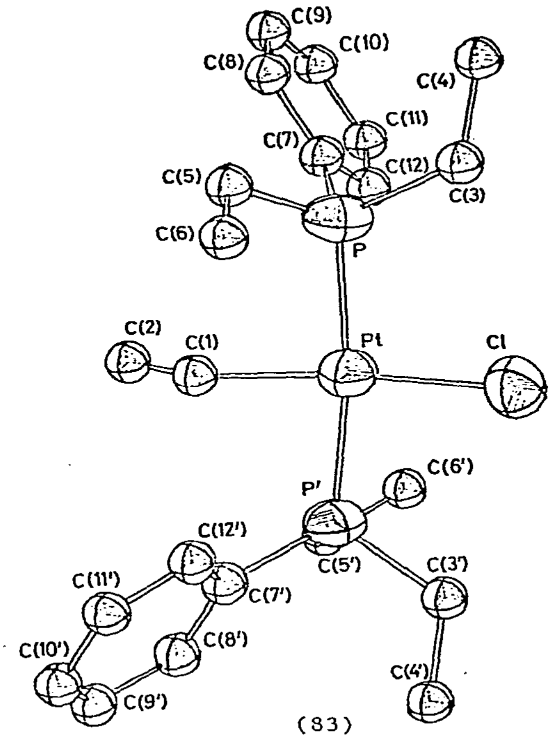
(82)

The crystal structure of trans-$PtCl(CH=CH_2)(PPhEt_2)_2$ (83) shows a distance for Pt-C of 2.03(2)Å, and a Pt-C=C angle of 127(2)Å [126]. An olefin palladium complex has also been obtained from palladium chloride and phenylmesityl acetylene [127]. In a similar reaction to the one described by Natile et al., [123], pyridine reversibly reacts with the coordinated olefin in



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(83)

<u>trans</u>-dichloro(π-ethylene)pyridine platinum(II) to give a σ-bonded adduct. Relative stabilities are discussed [128].

Nickel atom-perfluoroethylene matrix condensation reactions have been investigated. The complexes are considered to be of mixed perfluorometallocyclopropane-perfluoroethylene type. Details of the infrared and electronic spectra are given, in addition to calculations on such complexes [129]. Using a similar technique, Ozin <u>et al</u>., have also prepared complexes $Pd(C_2H_4)_n$ (n = 1, 2, 3) (84) [130]. Details of the spectral features are given, and extended

$$\text{"Pd"} + nC_2H_4 \longrightarrow Pd(C_2H_4)_n \quad (n = 1,\ 2,\ 3)$$

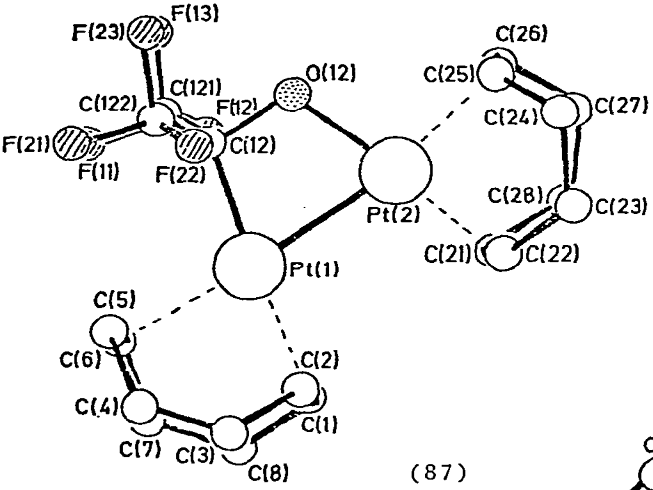
(84)

Hückel molecular orbital calculations have been carried out assuming C_{2v}, D_{2h} and D_{3h} symmetries for the molecules. Details of the preparation of $Pt(1,5\text{-}COD)_2$ (85) from $PtCl_2(1,5\text{-}COD)$ and lithium naphthalenide in the presence of 1,5-COD have been given. Similar reactions, along with olefin substitution reactions, have been used to

$$PtCl_2(1,5\text{-}COD) + 1,5\text{-}COD + Li_2C_8H_8 \longrightarrow Pt(1,5\text{-}COD)_2 + 2LiCl + C_8H_8$$

(85)

prepare the complexes [M(bicyclo(2.2.1]heptene)$_3$] (M = Pd, Pt), Pd(trans-cyclooctene)$_3$, Pt(trans-cyclooctene)$_3$, Pd(ethylene)$_3$, and Pt(ethylene)$_3$. The article gives details of the structure of [Pt(bicyclo[2.2.1]heptene)$_3$] (86) [131]. In the following article these workers investigate the reaction of Pt(1,5-COD)$_2$ with $(CF_3)_2CO$, $(CF_3)_2C{=}C(CN)_2$, and $(CF_3)_2C{=}NMe$ [132]. The structures of the complexes [Pt$_2${(CF$_3$)$_2$CO}(1,5-COD)$_2$] (87) and [Pt·C(CF$_3$)$_2$·O·C(CF$_3$)$_2$·O(1,5-COD)] (88) are given in the article. Reaction of Pd(1,5-COD) with C_2F_4 gives an octafluorodiplatinacyclohexane complex [Pt$_2$(μ-CF$_2$·CF$_2$)$_2$(1,5-COD)$_2$] (89). The 1,5-COD can be substituted for phosphines and arsines [133]. The complex



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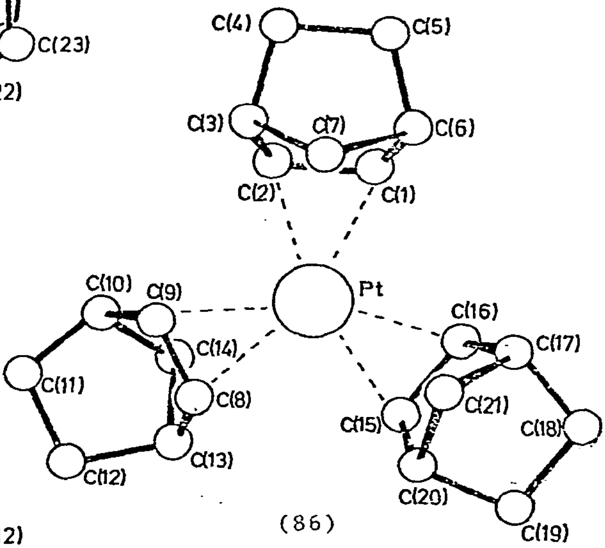

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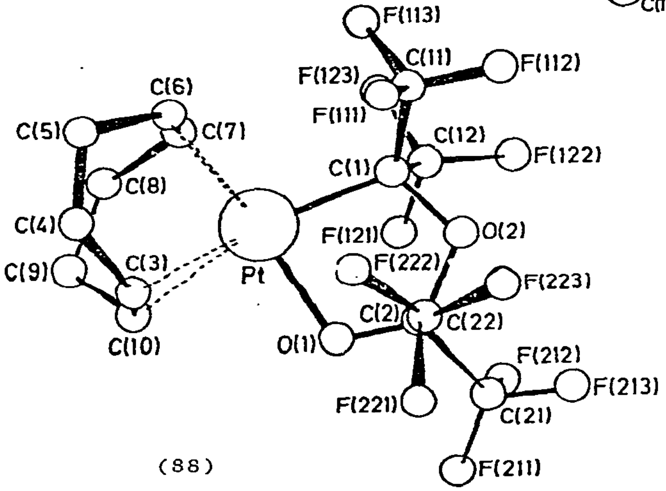

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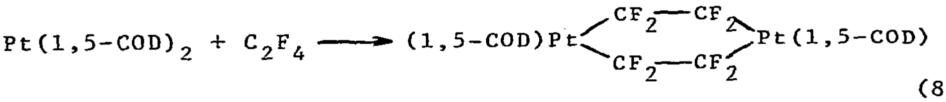
Pt(η-bicyclo[2.2.1]heptene)$_3$ reacts with C_2F_4 to give the mononuclear species $Pt(CF_2 \cdot CF_2)(C_7H_{10})_2$. In contrast, Pd(1,5-COD)$_2$ gives



$$Pt(1,5\text{-}COD)_2 + C_2F_4 \longrightarrow (1,5\text{-}COD)Pt\begin{matrix} CF_2-CF_2 \\ CF_2-CF_2 \end{matrix}Pt(1,5\text{-}COD)$$

(89)

(1,5-COD)Pd$(CF_2 \cdot CF_2)$Pd(1,5-COD) with C_2F_4. Other alkyl and vinyl compounds, along with their chemistries, are described. The complex Pt(1,5-COD)$_2$ reacts with the β-diketones, acetyl-, hexafluoroacetyl-, and trifluoroacetyl-acetone to give (cyclo-oct-4-en-1-yl)platinum

(90)

complexes (90) [134]. Protonation and other reactions of a similar type are also reported and discussed.

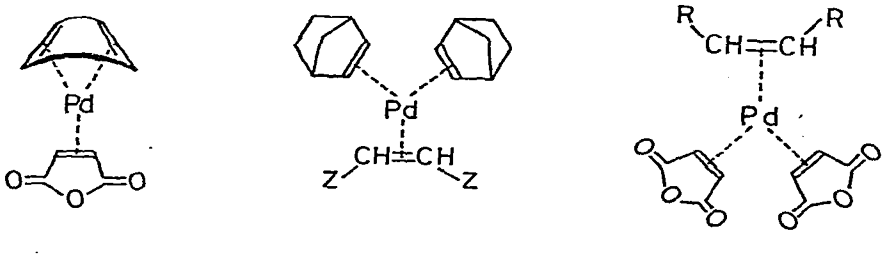
The complexes $Ni(C_2H_4)(PPh_3)_2$ and Ni(1,5-COD)(bipy) react with unsaturated compounds such as R_2CO, EtCHO, PhCH=NPh, PhN=NPh with displacement of the ethylene (91) [135]. Mixed olefin complexes of

$$Ni(C_2H_4)(PPh_3)_2 + L \longrightarrow NiL(PPh_3)_2 + C_2H_4$$

(91)

(L = R_2CO, EtCHO, PhCH=NPh, PhN=NPh)

Pd(0) have been prepared from $Pd_2(CHCl_3)$(dibenzylideneacetone)$_3$ or $Pd_3(CHCl_3)$(dibenzylideneacetone)$_3$ [136]. Complexes prepared in this manner are shown below (92); the olefins are 1,5-COD, NBD, dimethyl fumarate, maleic anhydride, norbornene, and cyclopentene.



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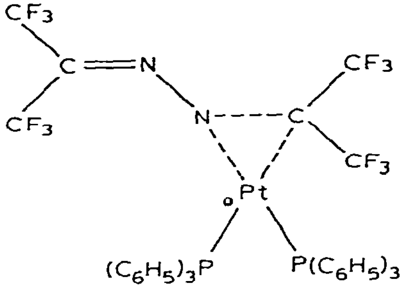
The crystal structure of hexafluoroacetone azine bis(triphenylphosphine)platinum shows the Pt atom σ-bonded to one C=N azine ligand forming a three-membered ring (93) [137]. Allylic ethers such as allyl phenyl ether and benzyl phenyl ether undergo allylic C-O bond scission with $Ni(1,5\text{-}COD)_2$ or $Ni(PPh_3)_4$. Added donors accelerate these cleavages (94) [138].



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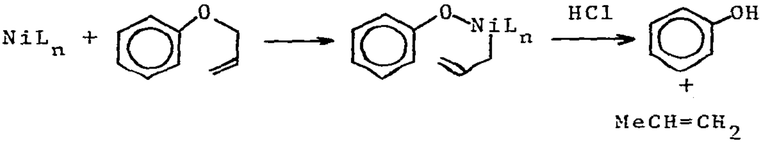
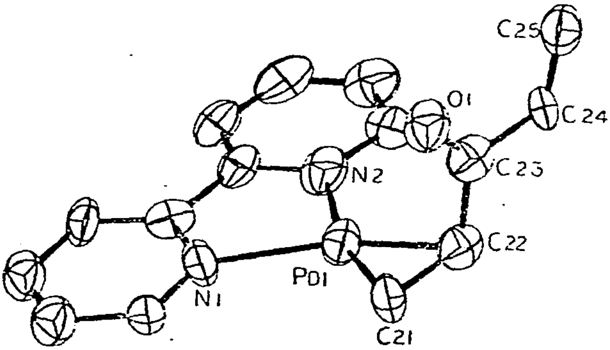


(94)

The direction of addition of a monoolefin to butadiene catalyzed by nickel complexes can be controlled by substituents on the olefin. The data are explicable in terms of the relative HOMO and LUMO energies in the different olefins [139].



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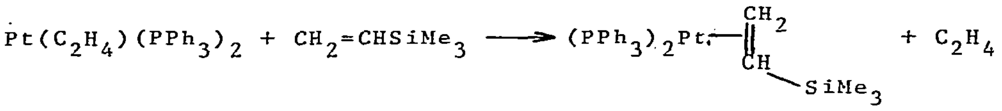
(95)

The structure of Pd(dibenzylideneacetone)(bipy) (95) has been published. The palladium is bonded to one bipyridyl and one dibenzylidene olefin [140]. Dimethyl fumarate, diethyl fumarate, dimethyl maleate, and maleic anhydride, react with $Pt(1,5\text{-}COD)_2$ and with

$Pt(C_2H_4)_3$ to give mixed olefin complexes of platinum(0) [141]. With 1,5-COD the complexes contain 1,5-COD and the second olefin, and with C_2H_4 the compounds contain C_2H_4 and two molecules of the second ligand. Complete substitution has also been effected. Preparation of the complex Pt(vinyltrimethylsilane)$(PPh_3)_2$ (96) [142] is reported. The synthetic procedure involves treating $Pt(C_2H_4)(PPh_3)_2$ with

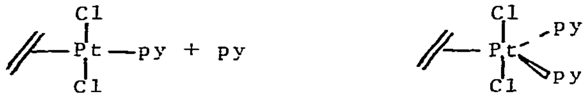


$$Pt(C_2H_4)(PPh_3)_2 + CH_2{=}CHSiMe_3 \longrightarrow (PPh_3)_2Pt{-}\overset{CH_2}{\underset{CH{-}SiMe_3}{\|}} + C_2H_4$$

(96)

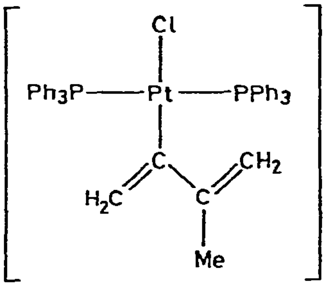
$CH_2{=}CHSiMe_3$. Upon irradiation, the complex $Pt(C_2H_4)(PPh_3)_2$ undergoes a variety of photochemistry depending on the solvent and on the wavelength used [143]. At 280 nm in $CHCl_3$ the product is $PtHCl(PPh_3)_2$, whereas in ethanol as solvent an ortho-metalated product is obtained. Ortho-metalation also occurs on photolysis at 254 nm in CH_2Cl_2 solvent. Electrochemical reduction of $PdCl_2$ in the presence of butadiene gives μ-1-3-η:6-8-η-octadienato bis(chloropalladium)polymer [144]. Treatment with Tlcp gives μ-1-3-η:6-8-η-octadienato bis(cyclopentadiene palladium).

NMR spectroscopy has been used to provide evidence for 5-coordinate pyridine-platinum(II) complexes (97). The resonance for the coordinated ethylene is very sensitive to pyridine concentration and the pyridine attacks the platinum rather than the coordinated olefin [145].



(97)

When *cis*-$PtCl_2(PPh_3)_2$ is treated in ethanol with hydrazine hydrate in the presence of isoprenylacetylene, the three main products are *trans*-$PtCl(CH_2{=}C{-}CMe{=}CH_2)(PPh_3)_2$ (98), *trans*-$Pt(CH_2{=}C{-}CMe{=}CH_2)(C{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2$ (99), and $Pt(CH{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2$ (100) [146]. Under similar conditions phenylacetylene gives *trans*-$Pt(C{\equiv}CPh)(CH_2{=}CPh)(PPh_3)_2$. The structures of (98) and (99) have been determined. The palladium diene complex $PdCl_2$(1,5-COD) has been used to prepare dithioacid complexes of palladium. A mixed



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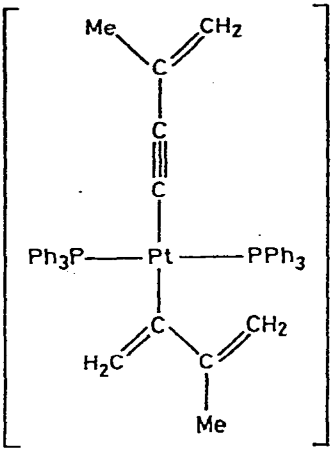

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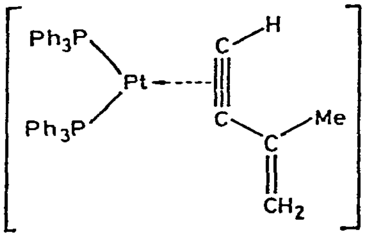

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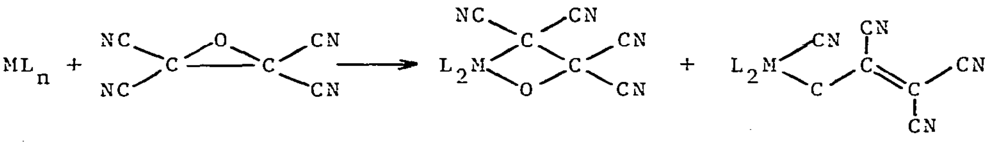
diethyldithiocarbamato olefin complex of palladium (101) has been prepared from an equimolar ratio of $PtCl_2$(1,5-COD) and $Na[S_2CNEt_2]$ [147]. A series of chelated complexes of Pd(II) have been obtained

$$PtCl_2(1,5\text{-COD}) + Na[S_2CNEt_2] \longrightarrow [\{PtCl(S_2CNEt_2)\}(1,5\text{-COD})] + NaCl$$

(101)

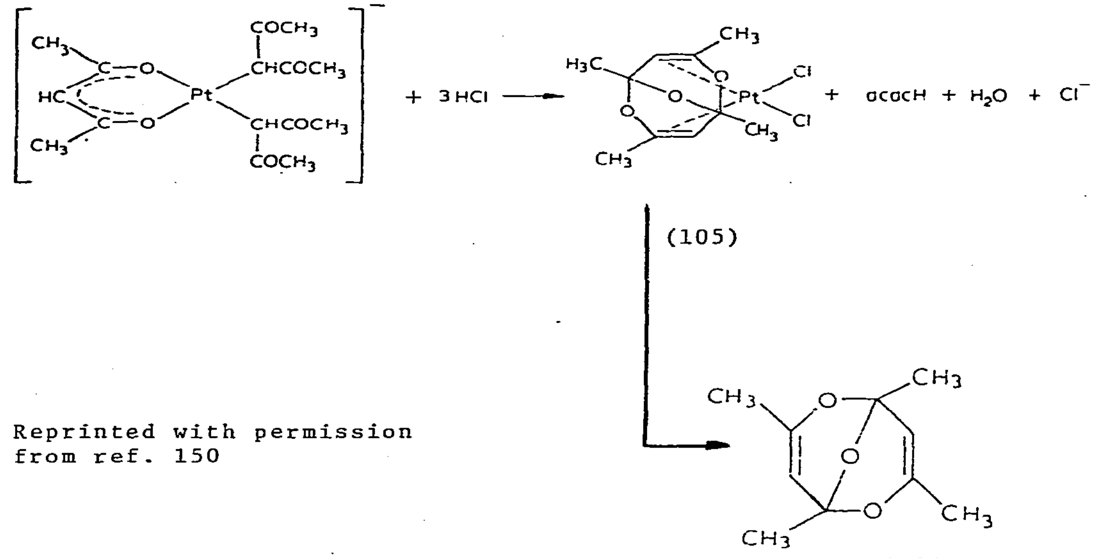
by nucleophilic attack on the coordinated olefin of 2,2,N,N-tetramethyl-3-buten-1-amine [148]. Tetracyanoethylene oxide reacts with tertiary phosphine and arsine compounds of Pd(0) and Pt(0) to give cyclic and acyclic complexes (102) and (103) [149].



(102) (103)

1,3,5,7-Tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-diene (104), a dimer of acetylacetone, is formed as a coordinated species through a Pt(II) promoted condensation reaction (105). The compound can be displaced from the complex by NaCN [150].

^{13}C NMR data are reported for a series of complexes <u>trans</u>-$[PtCl_2L(\underline{p}\text{-}Xpy)]$ (L = C_2H_4, $PhCH{=}CH_2$, t-Bu_2C_2, CO), <u>trans</u>-$[PtZ(\underline{p}\text{-}Xpy)(PPhMe_2)_2]BF_4$ (Z = Me, C≡CMe), and [PtCl(2-methoxy-5-cyclooctenyl)(p-Xpy)]. Small changes in the δC and $^{1}J_{^{195}Pt-^{13}C}$ data of the directly bound carbon atoms as X is varied have been interpreted in terms of slight fluctuations in the σ-donor component of these



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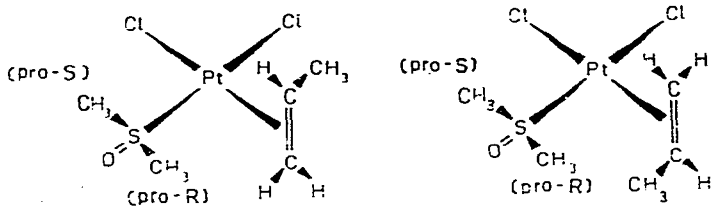
(104)

platinum–carbon bonds [151]. A useful method has been described to prepare complexes of type $PtCl_2$(DMSO)olefin [153]. The complex is fluxional, but upon cooling the ^{1}H NMR shows unequal population of the two stereoisomers (106). A second paper has been published by



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(106)

these authors to determine the extent to which chiral sulfoxide ligands are capable of distinguishing the prochiral faces of coordinated olefins. The absolute configurations of the coordinated olefins have been assigned. The amount of chiral induction is small, however quite large discrimination is observed for the olefinic rotation barriers of the R and S olefin diastereomers, the S olefin rotating more quickly than the R one [153]. A series of <u>cis</u>- and <u>trans</u>-[dichlorobenzylamine platinum(II)(chiral olefin)] complexes have been prepared [154]. The CD spectra have been interpreted on the basis of the individual contributions coming from the chiral centers already present in the free olefin and from the chiral centers formed in the complexation of the double bond. Platinum(II) complexes containing S,S- or R,R-trans-2-butene and various L-amino carboxylates, e.g. cis-(N,olefin)[PtCl(L-prolinate)(S,S-trans-2-butene)] and trans-(N,olefin)[PtCl(L-prolinate)(S,S- or R,R-trans-2-butene)] have been synthesized. The kinetics of the inversion reaction of the coordinated S,S- or R,R-trans-2-butene follows a second order rate law with respect to complex and free olefin [155]. The CD peaks of trans(N,ethylene)[PtCl(L-aminocarboxylate)C_2H_4] are characteristic of those complexes with asymmetric nitrogen [156]. Substitution of trans-2-butene for the olefin in PtCl(L-aminocarboxylate)(2-butene) and in $[PtCl_3(S,S\text{-trans-2-butene})]^-$ in organic solvents exhibits stereoselectivity such that substitution with retention of configuration proceeds faster than with inversion. Steric interactions seem to be responsible [157]. The structure of cis-$PtCl_2[(Me(O)S(p\text{-tol}))(Me_2CHCH{=}CH_2)]$ (107) shows the double bond of the coordinated olefin tilted by 5.7(6)Å from the perpendicular. The absolute configuration at the asymmetric carbon atom of the olefin is S [158]. Square planar complexes of Pt(II) containing η^2-olefins

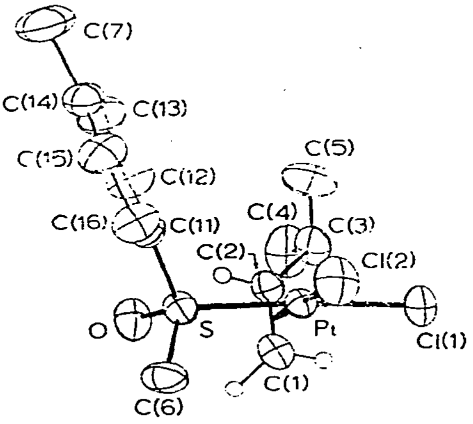

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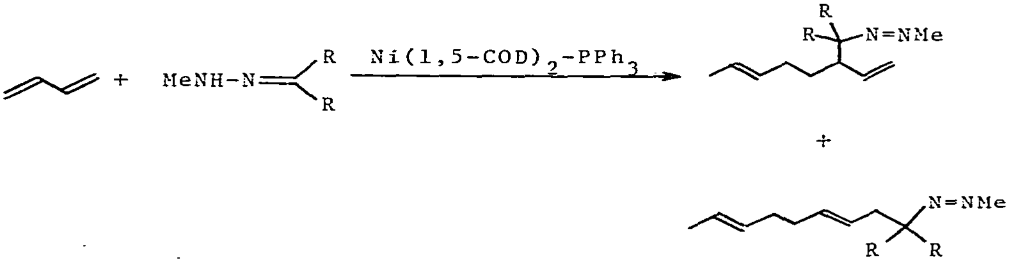
exhibit CD peaks at 20,000-30,000 and at 40,000 cm^{-1}. The (R,R)-configuration of the η^2-olefins exhibit a negative CD peak in the 40,000 region which is independent of metal or ligands [159]. ^{13}C and ^{195}Pt NMR spectra for the complexes trans-$PtCl_2(amine)(CH_2{=}CH_2)$ have been measured. For (S)-N-methyl-α-methylbenzylamine the two diastereomers present may be distinguished from each other by the values $^3J(Pt,C)$ [160]. Complexes $Ni(t\text{-}BuNC)_2(olefin)$ have been prepared for more than 150 olefins. Values for ν(C≡N) have been correlated to the electron-withdrawal properties of the olefins. Over 50 complexes of imines, diazenes, ketones, nitroso compounds, and acetylenes have been studied similarly. The relative M-olefin bond strengths have been measured calorimetrically, and the effects of changing substituents found to be cumulative [161].

Extended CNDO/2 studies have been carried out on η^2-C_2H_4Ni [162]. Non-empirical valence-electron calculations have been published on ethylene complexes of Pd(0) and compared with those of Ag(I). For Pd(0), electron transfer occurs mainly from Pd to ethylene with both σ^* and π^* orbitals accepting electrons, whereas with Ag(I) donation of electrons from ethylene π to Ag 5s and 5p orbitals is the dominant bonding feature [163]. The bonding of ethylene to Pd has been considered from the viewpoint of spectroscopy, where a close similarity is noted between the infrared spectra of the compound $(C_2H_4)Pd$ and ethylene adsorbed on palladium [164]. Using the SCF-Xα-SW method, the bonding of oxygen and ethylene to platinum(0) has been compared [165]. "Back-bonding" in $Pt(PH_3)_2O_2$ amounts to essentially complete ionic transfer of two electrons from the Pt $5d_{xy}$ to the in-plane O_2 π^* orbital with little covalent overlap between the two. Such overlap is appreciable in $Pt(PH_3)_2(C_2H_4)$ with the electrons receiving mainly in the d_{xy} orbital. A number of ethylene-nickel complexes with various additional ligands have been studied using ab initio MO-SCF calculations. The C=C bond is considerably lengthened on coordination. Attempts have been made to correlate the calculations with reactivity [166].

Sulfur heterocycles undergo desulfurization when treated with complexes such as $[Ni(1,5\text{-}COD)_2]_2$bipy. The reaction has been used with dibenzothiophene, phenoxathiin, and phenothiazine [167]. The mixture $Ni(1,5\text{-}COD)_2 + PPh_3$ has been used to effect the addition of methylhydrazones with butadiene. Correlation with R groups on the formation of complexes (108) is given [168]. Conjugated dienes are polymerized by $[NiI(\pi\text{-}crotyl)]_2$ and the end unit of the propagating polymer chain is a π-allylic structure [169].



(108)

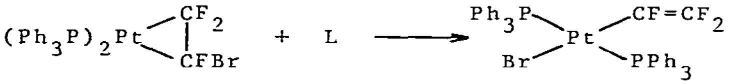
Trans-$PtCl(CCl{=}C(H)Cl)L_2$ (L = $PMePh_2$) reacts with acids HX to give an equilibrium mixture of vinylic isomers (109) [170]. The rate of isomerization is a function of X, and occurs much faster in CD_2Cl_2 than in benzene. Similar systems and reactions have been studied, and the processes are explained in terms of a cationic platinum-chlorocarbene intermediate. Alkenyl ($CH=CH_2$, $CF=CF_2$) or alkynyl ($C\equiv CPh$) derivatives of trimethyltin are very effective for the synthesis of mono-organovinyl platinum(II) complexes (110) [171]. The reactivity order for R, $-C\equiv CPh > -CF=CF_2 > -CH=CH_2$ is also found for the oxidative addition of $SnMe_3R$ to Pt(0) to give cis-$Pt(SnMe_3)RL_2$. Acetylide complexes, and reactions with aromatic isonitriles, are also discussed. A series of compounds trans-$PtX(CF=CF_2)(PPh_3)_2$ (111) have been prepared by treating the π-olefin complex $Pt(CF_2=CFBr)(PPh_3)_2$ with ligands such as $CF_3CO_2^-$, acac$^-$, CN^-, SCN^-, SO_2 [172]. The compound acetylacetonato (1,cis-3,trans-tetraphenyl-4-ethoxybutadiene-1-yl)dimethylphenylphosphine palladium(II) (112), prepared from $PdCl(OEt)C_4Ph_4$ and Tl acac followed by $PPhMe_2$, is a vinyl complex with a distance Pd-C of 2.004(5)Å. The structure consists of two independent molecules of opposite chirality in each asymmetric unit [173]. The preparations of a series of 1-platinacyclopent-4-ene-2,3-dione complexes (113) with L = $AsPh_3$, PPh_3, $PPhEt_2$, PEt_3, $PMePh_2$, $PPhMe_2$, $P(OPh)_3$, dpe, py, bipy and phen are described [174].

(109)

$$\underline{cis}\text{-}PtCl_2L_2 + SnMe_3R \longrightarrow \underline{trans}\text{-}PtClRL_2 + SnMe_3Cl$$

(110)

(L = tertiaryl phosphine)



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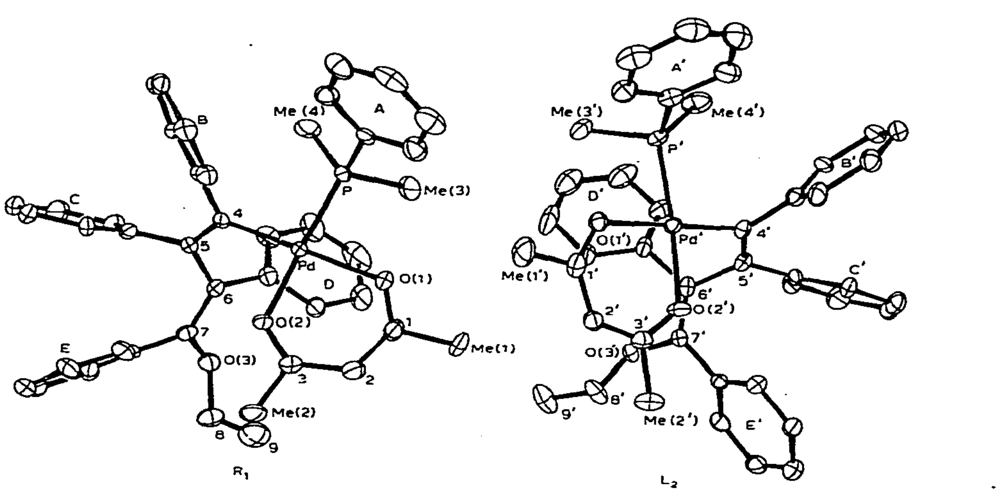

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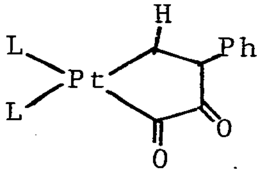
VII. Metal acetylenes and acetylides

The crystal structure of $Pt(CF_3C{\equiv}CCF_3)(PCy_3)_2$ (114) shows a bond length for C≡C of 1.260(10)Å, and the *cis*-bent geometry about the acetylene with an angle of 45.5(8)Å [175]. Treating $Pt(1,5\text{-}COD)_2$ with $CF_3C{\equiv}CCF_3$ affords $Pt\{C(CF_3)=C(CF_3)\}(1,5\text{-}COD)$, which reacts with PPh_3, CO, or $CF_3C{\equiv}CCF_3$ to give $Pt\{C(CF_3)=C(CF_3)\}(PPh_3)_2$, $Pt\{C(CF_3)=C(CF_3)\cdot Pt\cdot C(CF_3)=C(CF_3)\}(1,5\text{-}COD)$, and $Pt\{C(CF_3)=C(CF_3)\cdot Pt\cdot C(CF_3)=C(CF_3)\cdot Pt\cdot C(CF_3)=C(CF_3)\cdot C(CF_3)=C(CF_3)\}(1,5\text{-}COD)_2$, containing 3-, 4-, 6-, and 8-membered rings [176]. The



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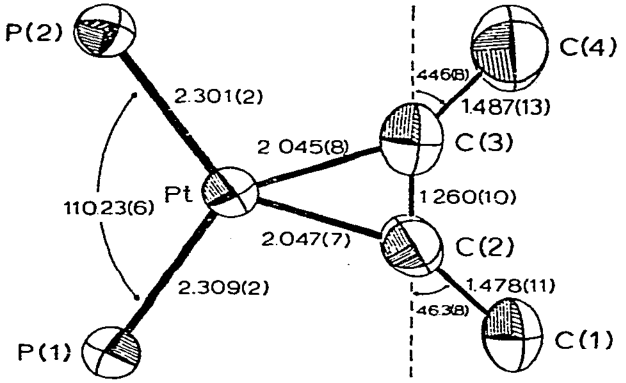

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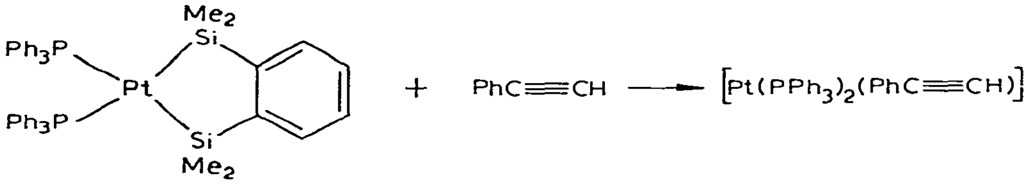
triplatinum compound has been established structurally. This complex is formed from $Pt(C_2H_4)_3$ and $CF_3C{\equiv}CCF_3$. Treating $[Pt{\cdot}C(CF_3)_2O{\cdot}Pt(1,5\text{-}COD)_2]$ with $CF_3C{\equiv}CCF_3$ gives $Pt\{C(CF_3){=}C(CF_3){\cdot}Pt{\cdot}C(CF_3){=}C(CF_3)\}(1,5\text{-}COD)_2$. Structural work shows a 6-membered ring with two Pt atoms. The complex $Pt(PhC{\equiv}CH)(PPh_3)_2$ (115) has been prepared by treating $Pt(\underline{o}\text{-}C_6H_4(SiMe_2)_2)(PPh_3)_2$ with $PhC{\equiv}CH$ [177]. When acetylene is passed through a benzene solution of *cis*-$Pt(SiPh_2H)_2(PPhMe_2)_2$ the compound (116) is obtained. Treating nickelocene with $Ph_2PC{\equiv}CCF_3$ gives 6 products, one of which is $[(\eta^5\text{-}cp)Ni]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$ (117) [178]. The binuclear complex contains two nickel atoms asymmetrically bridged



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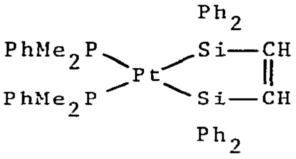

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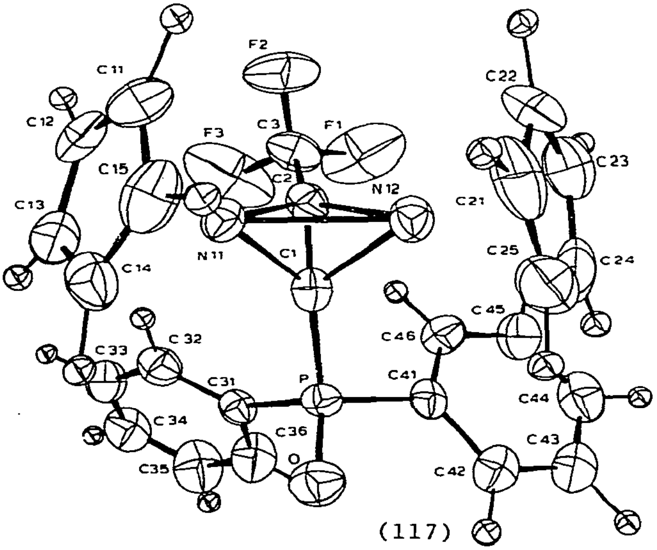

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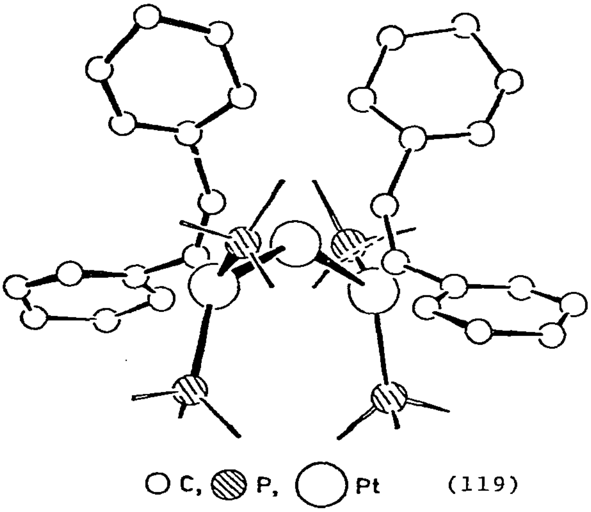
by a π-bonding acetylene. A bridging acetylene complex $[Pd(\eta^5-C_5Ph_5)]_2C_2Ph_2$ (118) has been obtained from $Pd(OAc)_2$ and C_2Ph_2. Interestingly the formation of pentaphenylcyclopentadiene complexes from C_2Ph_2 involves C≡C cleavage at some stage of the reaction, one half being lost as $ArC(OR)_3$. The reactions with NO and HX are described [179]. The structure of the acetylene bridged complex is

$$Pd(OAc)_2 + C_2Ph_2 \longrightarrow [(\eta^5-C_5Ph_5)Pd]_2C_2Ph_2 + \text{other products}$$

(118)

given. Di- and tri-platinum, and di-nickel acetylene complexes, $[Pt_2\{\mu_2(\eta^2-C_2Ph_2)\}(\eta^2-C_2Ph_2)(PPh_3)_2]$, $[Ni_2\{\mu_2(\eta^2-C_2(SiMe_3)_2)\}(1,5\text{-}COD)_2]$, and $[Pt_3\{\mu_2(\eta^2-C_2Ph_2)\}_2(PEt_3)_4]$ (119) have been prepared [180]. The structure of (119) shows a Pt·Pt·Pt sequence bridged transversely by two diphenylacetylene ligands.



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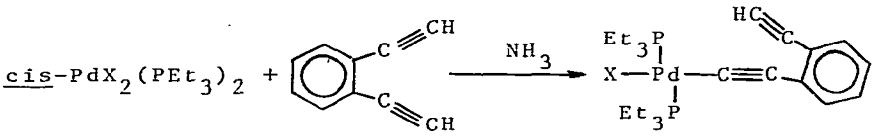
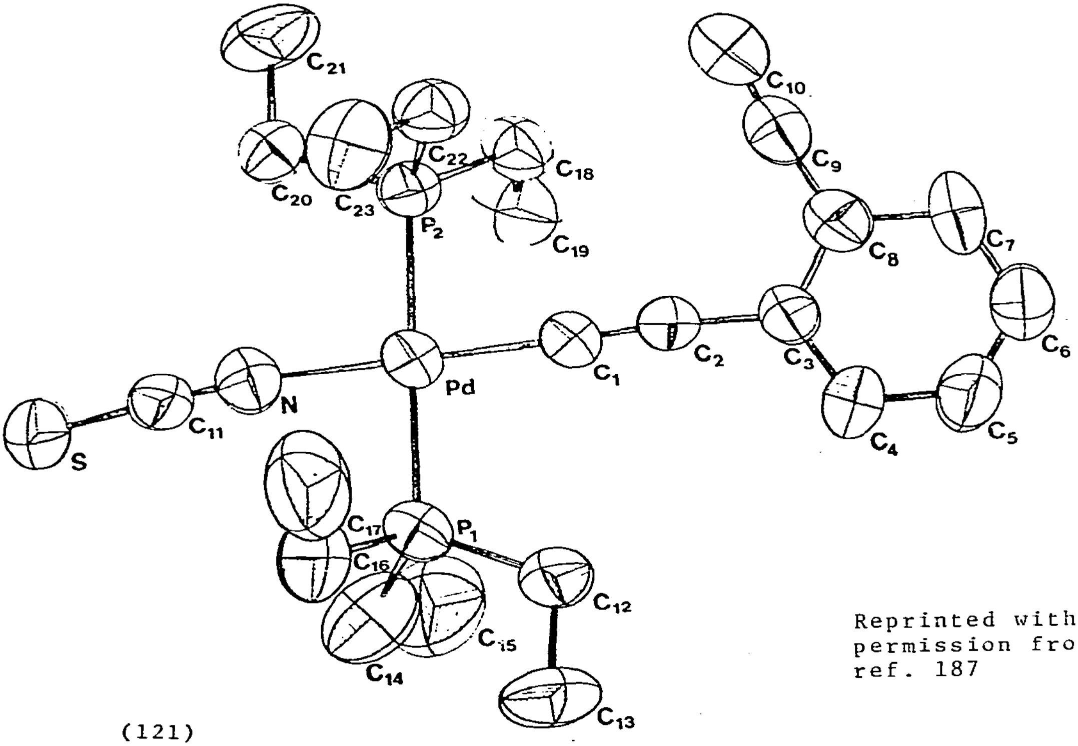
The integrated molar absorption coefficients $\bar{A}_{int}$ of the C≡C stretching frequency of the coordinated alkynes of Rh, Ir, Ni, and Pt complexes of $C_2(CF_3)_2$, C_2Ph_2, and hexyne have been measured. A relative scale of donor-acceptor interactions in the complexes has been calculated from the measured values of $\bar{A}_{int}$ and $\Delta(\nu^2) = \nu^2(\text{free alkyne}) - \nu^2(\text{coordinated alkyne})$ [181]. The structure of <u>cis</u>-$Pt(C{\equiv}CPh)_2(PPh_3)_2$ has a planar <u>cis</u> geometry about platinum [182]. The structure of <u>trans</u>-$(C{\equiv}CPh)(styryl\text{-}C^2\text{-})(PPh_3)_2$ shows that, in agreement with the IR and NMR measurements, 1-alkene(styrene) and 1-alkyne are σ-bonded to Pt in a <u>trans</u> configuration with the styryl group interacting through C^2. The coordination shows a small tetrahedral distortion from planar [183]. The structure of trans-PtCl(isopropenylacetylido)$(PPh_3)_2 \cdot 1/2\ C_6H_6$ shows a σ-bonded acetylido ligand. The Pt-C distance is 2.14(3)Å, and isopropenylacetylene, which is planar, is tilted by 61° with respect to the coordination plane [184]. The structure of the same complex with 2/3 $CHCl_3$ solvated has also been solved [185]. Treating the compound trans-$PdX_2(PEt_3)_2$ with solutions of o-diethynylbenzene in liquid ammonia gives complexes trans-PdX(o-$C_2C_6H_4C_2H$)$(PEt_3)_2$ (X = Cl, Br, I) (120) [186]. The corresponding pseudohalide compound can be prepared by substitution. The molecular structures have been determined by ^1H and ^{31}P NMR spectroscopy, and the N-thiocyanato complex by X-ray methods. In the following paper the structure of the -NCS compound



(120)

(121) shows a Pd-C distance of 1.952(7)Å, which is only 0.04Å shorter than a single bond [187]. Transition metal σ-alkynyl complexes have



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(121)

been prepared in high yield by the reaction of metal halides and acetylenes in the presence of a catalytic amount of CuI in diethylamine [188]. A range of Ni, Pd and Pt acetylide complexes have been obtained in this manner. The addition of $C_2(CO_2Me)_2$ to trans-$PdH(C{\equiv}CPh)(PEt_3)_2$ gives trans-$Pd(C{\equiv}CPh)\{(MeO_2C)HC{=}C(CO_2Me)\}(PEt_3)_2$

$$\text{\underline{trans}-}PdH(C{\equiv}CPh)L_2 + C_2(CO_2Me)_2 \rightarrow Pd(C{\equiv}CPh)\{(MeO_2C)HC{=}C(CO_2Me)\}L_2$$

$$(L = PEt_3) \qquad\qquad (122)$$

(122). The Pd-C bond lengths are in the 2.03(2)Å to 2.06(2)Å range [189].

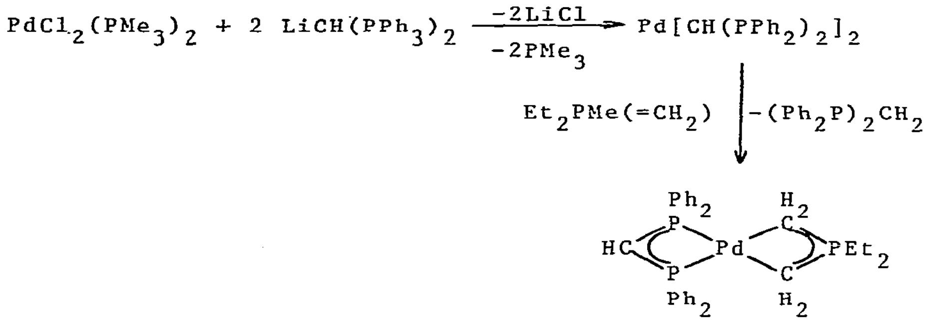
The reactions of complexes trans-$PtX(C{\equiv}CR)L_2$ (R = H, Me, CF_3; X = $C{\equiv}CR$, Cl; L = $PPhMe_2$, $AsPh_3$) with substrates A-B are discussed [190]. Four types of reaction occur: (i) oxidative addition (ii) insertion (e.g., $C_2(CN)_4$) (iii) attack at $-C{\equiv}C-R$ to give vinylplatinum(II) compounds (e.g. CF_3COCl, NOCl) (iv) formation of 1:1 π complexes (e.g. $(CF_3)_2CO$). A wide range of complexes $NiXYL_2$ have been used in the polymerization and aromatization of phenylacetylene. The reaction rate, the yield of cyclic trimers, and the ratio of 1,2,4/1,3,5-triphenylbenzene depend on both phosphine and anion [191].

VIII. Metal allyls

A new π-allyl complex of palladium (123) has been obtained from $[PdCl(\eta^3-C_3H_5)]_2$ and $Pb[N(SiMe_3)_2]_2$ [192]. Although the complexes are of the ylide type, the palladium complexes of diphosphinomethanide-phosphoniumbismethylide (124) resemble an allyl type of bonding [193]. The complex (η^3-1-methylene-3-methylcyclohexyl)triphenylphosphine palladium (125) has been prepared from the reaction of the chloro bridged dimer with PPh_3 [194]. The reaction of $Pd(\eta^5-cp)$(2-R allyl) with tertiary phosphines or phosphites in a 1:1 molar ratio yields dinuclear complexes $Pd_2(\eta^5-cp)$(2-R allyl)L_2. The crystal structure of the complex with R = Me and L = PPh_3 (126) shows that the cyclopentadienyl, as well as the allyl ligand, is bonded in a sandwich manner to the Pd-Pd unit [195]. π-Allylic complexes of Pd(II) have been prepared with amino acid anions as

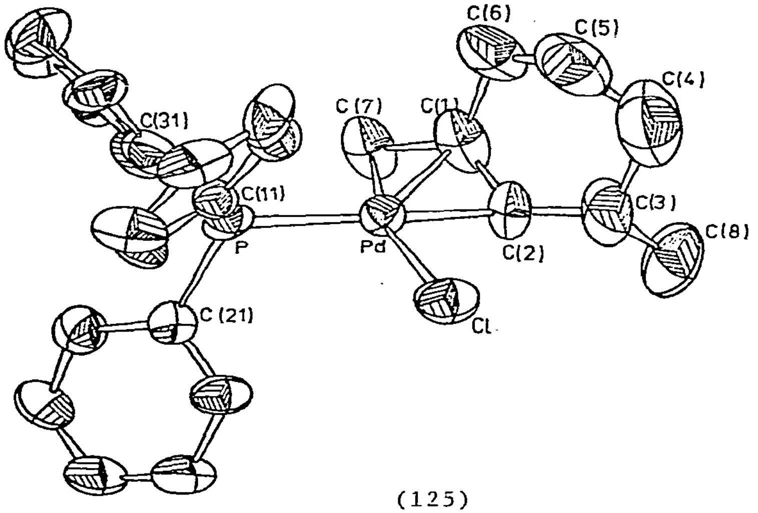
$$[PdCl(\eta^3-C_3H_5)]_2 + Pb[N(SiMe_3)_2]_2 \rightarrow PdCl(\eta^3-C_3H_5)\{Pb[N(SiMe_3)_2]\}_2$$

$$(123)$$



(124)

bidentate ligands [196]. π-Allyl complexes of palladium have also been prepared from calciferol, ergosterol, 3-*epi*-ergosterol, and 7-dehydrocholesterol [197]. The π-allylic dimers from methylenecyclopentane, methylenenorbornane, and methylenecamphor have been reported in an article focussed on the palladium(II) catalyzed ring expansion of methylencyclobutane and its 3-substituted derivatives [198]. Cyclization of the dynamic σ,π-complex [{Pd(α- β-$C_5Me_5CHPhCH_2$)Cl}$_2$] (1α,β) leads to the bicyclo[3.2.0] hept-2-enylpalladium complexes [Pd(γ-$C_5Me_5CHPhCH_2$)Cl]$_2$ (1 γ, phenyl *endo* to Pd) and [Pd(δ-$C_6Me_5CHPhCH_2$)Cl]$_2$ (1 δ, phenyl *exo*). The series of complexes are shown (127) [199]. The syntheses and temperature-dependent ^1H and ^{13}C NMR spectra of the complexes [Pd(η^3-allyl)(η^4-diene)]PF_6 (allyl = C_3H_5, 1-MeC_3H_4, 2-MeC_3H_4, 2-PhC_3H_4; diene = cyclooctatetraene; allyl = 2-MeC_3H_4, diene = 1,5-COD; hexamethylbicyclohexa[2.2.0]diene, 1,5-hexadiene, cycloheptatriene),



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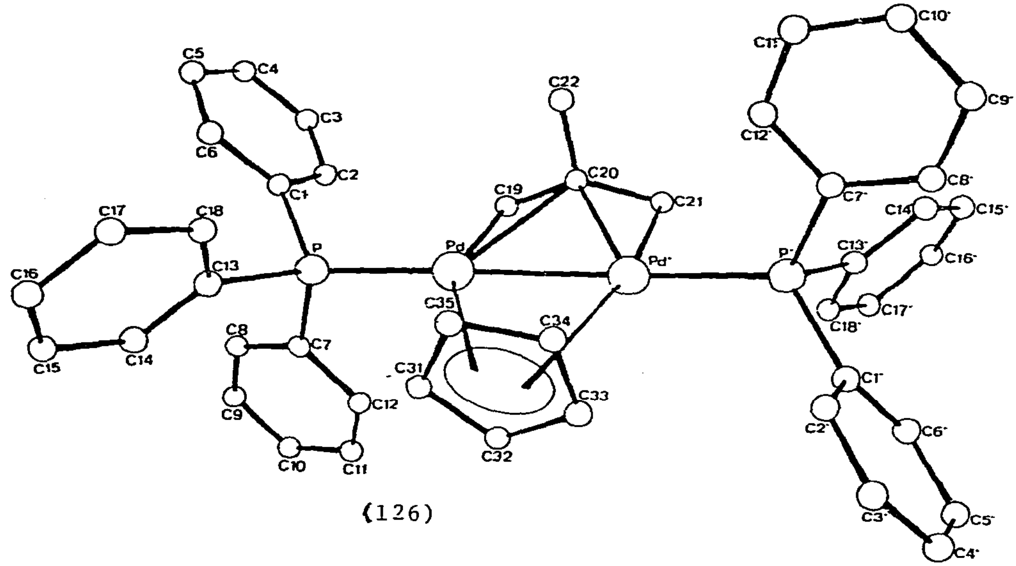

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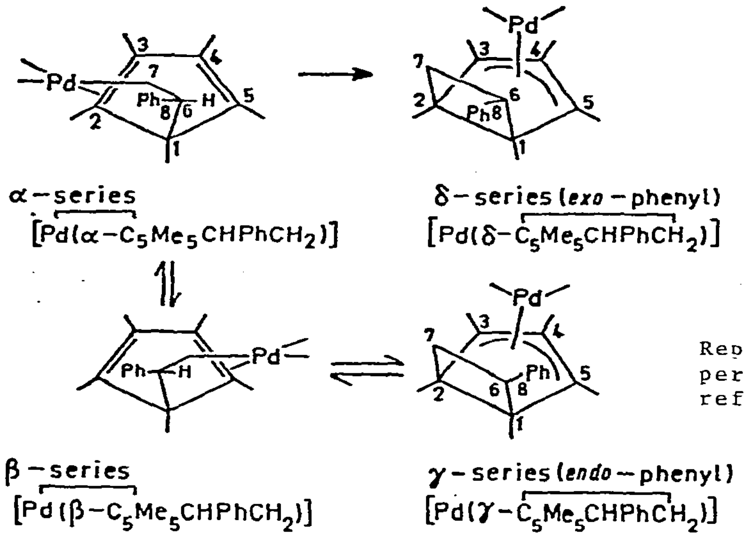
$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, and $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(\eta^4\text{-}diene)]PF_6$ are reported [200]. Nonrigidity occurs and mechanistic explanations are discussed.



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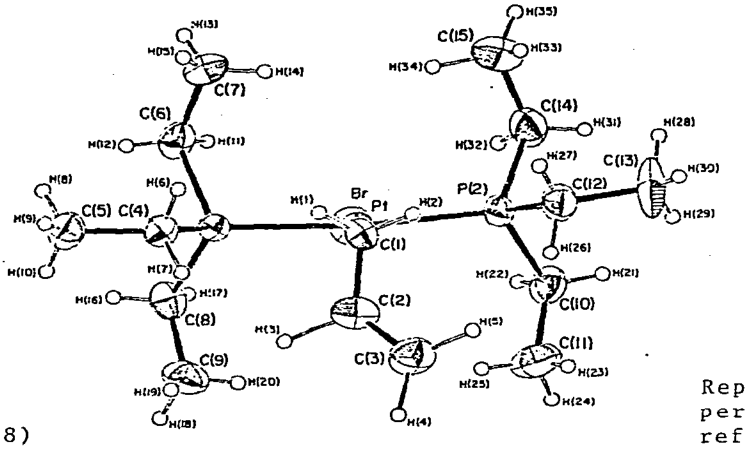
The structure of the η^1-allyl complex trans-$PtBr(\eta^1\text{-}C_3H_5)(PEt_3)_2$ (128) shows a Pt-C distance of 2.086(7)Å. There is no interaction between the double bond and the platinum atom [201]. The reaction of $[PtCl(allyl)]_4$ with isocyanides gives dimeric σ-allyl complexes $[PtCl(CNR)(\sigma\text{-allyl})]_2$ (R = Me, Cy, 2,6-$Me_2C_6H_3$) (129). Upon dissolution in dichloromethane, these compounds give the π-allyl complexes (130), which react with isocyanides to give $PtCl(\sigma\text{-allyl})(CNR)_2$



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(131) [202]. Stable σ-allyl complexes of platinum (132) have been prepared by the oxidative addition of allylic halides to $Pt(PEt_3)_4$

$$[PtCl(allyl)]_4 + 4\ CNR \longrightarrow [PtCl(\sigma\text{-}allyl)CNR]_2 \qquad (129)$$

$$[PtCl(\sigma\text{-}allyl)CNR] \xrightarrow{CH_2Cl_2} PtCl(\pi\text{-}allyl)CNR \qquad (130)$$

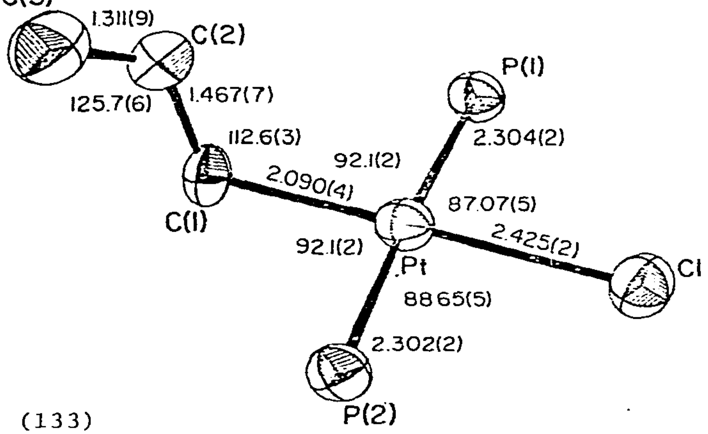
$$PtCl(\pi\text{-}allyl)CNR + CNR \longrightarrow PtCl(\sigma\text{-}allyl)(CNR)_2 \qquad (131)$$

[203]. The structure of trans-$PtCl(\eta^1\text{-}allyl)(PPh_3)_2$ (133) shows an angle between the plane of the allyl group and the coordination plane

$$PtL_4 + CH_2{=}CHCH(R)Cl \longrightarrow PtCl(\sigma\text{-}CH(R)CH{=}CH_2)L_2 + 2L$$

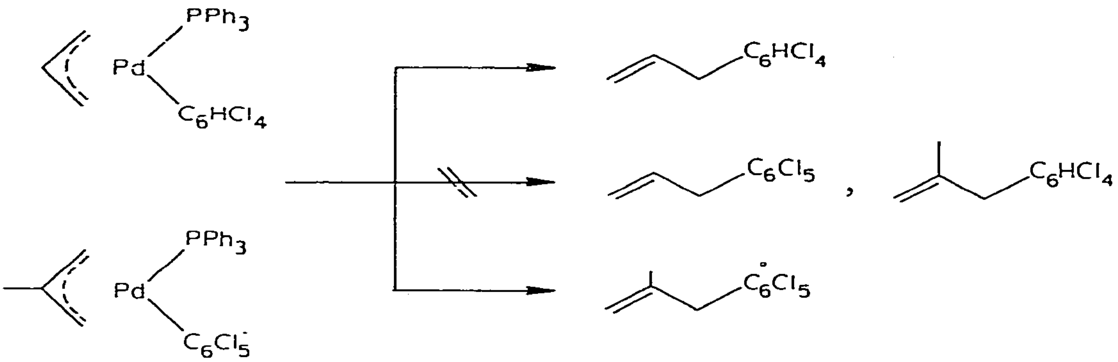
(132)

L = PEt_3; R = H, Me



(133)

of 66°. It is suggested that the fluxionality of [Pt(η^3-allyl)(PPh_3)$_2$]Cl in solution involves a short-lived σ-allyl intermediate [204]. Complexes Pd(Ar)(π-allyl)L (134) (Ar = C_6Cl_5, 2,3,5,6-C_6HCl_4; allyl = CH_2=$CMeCH_2$, MeCH=$CHCH_2$, EtO_2CCH=$CHCH_2$; L = PPh_3, $SbPh_3$) have been prepared. The compounds are particularly useful for studying allylic alkylation via π-allylpalladium complexes. Reductive elimination proceeds by a unimolecular concerted pathway to give, in a regio- and stereo-selective fashion, quantitative yields of allylpolychlorobenzenes [205]. When these compounds are treated with tertiary phosphines, stable σ-allyl complexes of the form trans-M(Ar)(σ-allyl)L_2 (135) (M = Pt, Pd; Ar = 2,3,5,6-C_6HCl_4, C_6F_5; allyl = CH_2=$CHCH_2$, MeCH=$CHCH_2$, CH_2=$CMeCH_2$; L = PPh_3, $PPhMe_2$ are obtained. The order for the ease of formation is given, and it is proposed that the occurrence of the trans structure in such σ-allyl complexes is a result of the thermodynamic, but not necessarily kinetic, control. The cis-σ-allyl complexes M(σ-CH_2CH=CH_2)Ar(dpe) have been prepared [206].



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$$\text{M(Ar)(}\pi\text{-allyl)L} + \text{L} \longrightarrow \underline{\text{trans}}\text{-M(Ar)(}\sigma\text{-allyl)L}_2$$

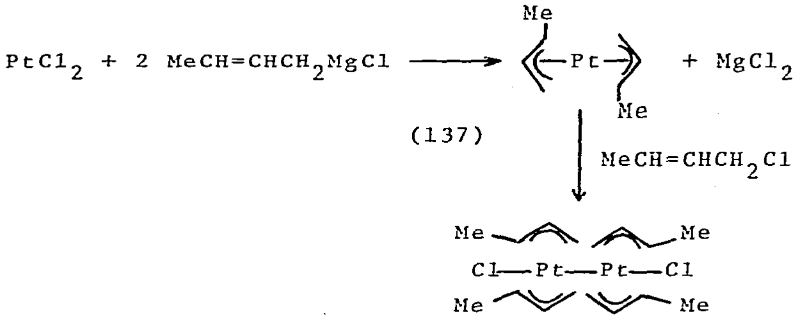
(135)

From enthalpies and equilibrium constants obtained calorimetrically for the reaction of [PdCl(π-Me allyl)]$_2$ with bases to give (136), the palladium Lewis acid has been characterized in terms of its E_A and C_A parameters [207]. For adduct formation with phosphines or phosphites the extra stabilization energy is attributed to

$$[\mathrm{PdCl}(\pi\text{-Me allyl})]_2 + 2\mathrm{B} \longrightarrow 2\ \mathrm{PdCl(B)}(\pi\text{-Me allyl})$$

(136)

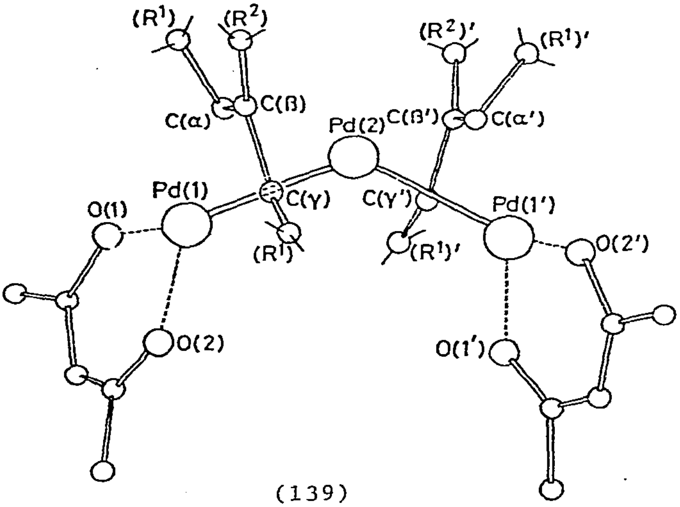
stabilization from π-back-bonding. Treating PtCl$_2$ with crotylmagnesium chloride gives Pt(π-crotyl)$_2$ (137). Treating this compound with crotyl chloride gives the dimeric complex (138) [208].



(137)

(138)

Dibenzylideneacetonepalladium(0) and -platinum(0) complexes react with triarylcyclopropenium bromides to give the ring opened trinuclear complexes $\mathrm{M_3Br_2(C_3R_3)_2}$. The acac derivative $[\mathrm{Pd_3\{C_3Ph}(\underline{p}\text{-}\mathrm{MeOC_6H_4})_2\}_2(\mathrm{acac})_2]$ (139) shows a bent Pd-Pd-Pd skeleton with η^3-$\mathrm{C_3R_3}$ ligands bridging each pair of palladium atoms such that the $\mathrm{C_3}$ plane intersects the Pd-Pd bonds [209]. A series of η^3-allyl complexes of nickel have been obtained from Ni(CO)$_4$. Useful preparations are described with tetramethylthiourea as a neutral leaving group [210]. Details



(139)

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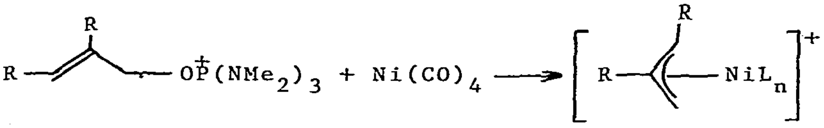
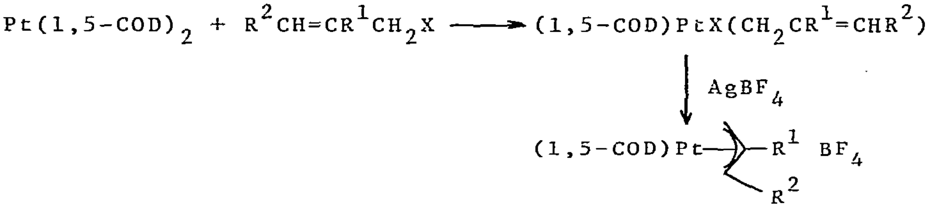
of the preparation of nickel allyls (140) from allyloxytris(dimethylamino)phosphonium salts and $Ni(CO)_4$ have been published [211]. π-Allylnickel complexes have been prepared by treating $Ni(CO)_4$ on



(140)

Al_2O_3 with allene [212]. Allyl halides oxidatively add to Pt(1,5-COD)$_2$ to give monomeric η^1-allylic complexes $[PtX(CH_2R^1{=}CHR^2)(1,5\text{-}COD)]$ (141) (R^1 = H, R^2 = H, Me, Ph; X = Cl, Br. R^1 = Me, R^2 = H, X = Cl, Br. R^1 = Cl, R^2 = H, X = Cl) [213]. The compounds react with $AgBF_4$ to give η^3-allylic compounds $[Pt(CH_2CR^1CHR^2)(1,5\text{-}COD)]BF_4$ (142). The 1,5-COD ligand is readily displaced by tertiary phosphines, arsines, stibines, phosphites, pyridine or isocyanides. The



(141)

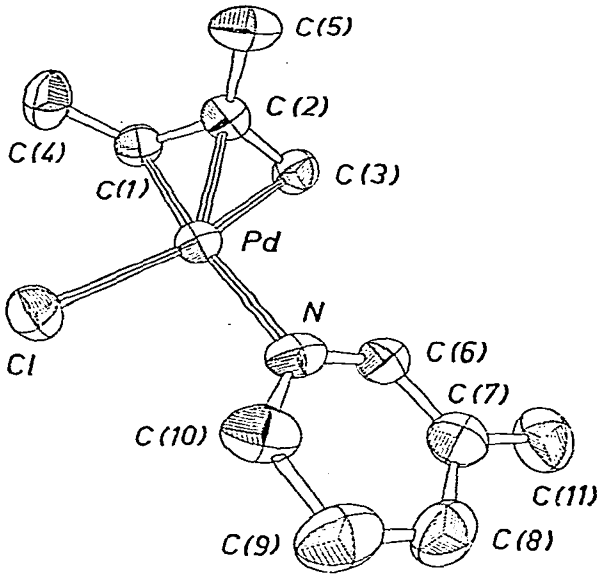
(142)

η^1-η^3 dynamic behavior is discussed. The reactions of cationic vinylplatinum complexes $[Pt(R^1C{=}CHR^2)(PEt_3)_2(acetone)]PF_6$ with allene and activated acetylenes give π-allyl (143) and σ-butadienyl complexes, respectively. Similar reactions with PdMe(X)dpe are reported and the factors affecting these insertion reactions are discussed

$$PtX(R^1C{=}CHR^2)(PEt_3)_2 + CH{=}C{=}CH_2 \longrightarrow [Pt(\eta^3\text{-}CH_2CH(R^1C{=}CHR^2)CH_2)(PEt_3)_2]X$$

(143)

[214]. The structure of PdCl(π-1,2-dimethylallyl)picoline (144) shows the first example of a coplanar pyridine in a palladium(II) complex [215]. The concepts of the temperature-dependent processes occurring in π-allylic palladium chlorides and heteroaromatic bases have been investigated. Differences in behavior are noted between hindered and unhindered bases [216].



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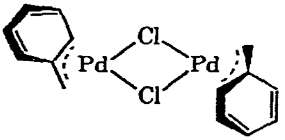
Chloro[N,3'-5'-η'-(4'-methylpentenyl)quinoline-2]palladium has been prepared [217]. The NMR spectrum has been used to aid distinction of <u>cis</u>/<u>trans</u> isomers of other non-bridged π-allyl chloropalladium complexes with nitrogen bases. An attempt to use mass spectroscopy to prove the exchange of allyl groups in mixtures of bis-π-allyl palladium complexes was unsuccessful because of the possible occurrence of such an exchange during the mass spectroscopic experiment itself [218].

Reductive decomposition of the π-allyl complex $[PdCl(CH_2CMeCH(CH_2OMe))]_2$ (145) with NaOMe in MeOH at 20° gives 47% $Me_2C{=}CHCH_2OMe$, 15% $CH_2{=}CMeCH_2CH_2OMe$, 14% $CH_2{=}CMeCH_2CH(OMe)_2$, 11% $Me_2C{=}CHCH(OMe)_2$, 8% $Me_2CHCH{=}CHOMe$ and 5% unidentified products [219]. A similar reductive decomposition of the compound has been effected with HCO_2Na in MeOH [220]. In a deuterium labelling experiment involving these decompositions it has been concluded that a monomeric Pd allyl complex is formed. This methoxypalladium complex undergoes elimination to form a hydrido palladium intermediate with subsequent transfer of the hydride from palladium to the allyl [221]. The reaction of this allyl (145) in MeOH has been investigated. Extinction coefficients and equilibrium constants have been measured [222].

Oxidative addition of benzyl chloride and substituted benzyl chlorides to Pd atoms gives η^3-benzylpalladium chloride dimers (146). Complex (146) adds 4 molecules of PEt_3 by first forcing the η^3-benzyl-η^1-benzyl transformation, and then breakage of the Pd-Cl bridges, to form trans-$PdCl(\eta^1\text{-benzyl})(PEt_3)_2$ (147) [223]. Similar η^3-benzyl compounds are prepared from 4-methylbenzyl chloride, 2-chloro-2-phenyl-1,1-trifluoroethane, and 3,4-dimethylbenzyl chloride.



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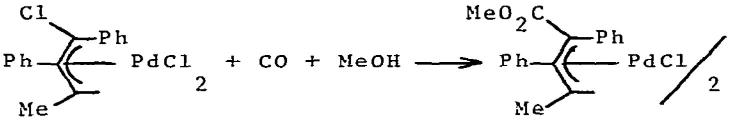
(146)

$$(145) + 4PEt_3 \longrightarrow 2\ PdCl(\sigma\text{-}CH_2Ph)(PEt_3)_2$$

(147)

Fluxionality and rotation is discussed. The ^{13}C NMR spectra of 13 acyclic and cyclohexenyl π-allyl palladium chloride dimers show the signals for the central carbons of the π-allyl palladium moiety displaced upfield by 8.0 - 25.0 ppm, and those for the terminal carbons by 34.9 - 55.9 ppm, compared to the corresponding olefins [224]. The reaction of 1-chloro-1,2-diphenyl-3-alkyl-π-allylpalladium complexes with CO gives methoxy esters, lactones and carbomethoxy-π-allylpalladium complexes (148) [225]. The reaction of 2-t-butyl-1,3-butadiene with π-allylic palladium chlorides has been reported [226]. The 2-chloroallyl complex gives a π-allylic complex with an open-chain structure in which the butenyl group is in the anti-position (149). Allyl-, 1-carbomethoxyallyl-, methallyl-, and 1-carbomethoxymethallyl-palladium chlorides give 6-membered cyclic complexes. The



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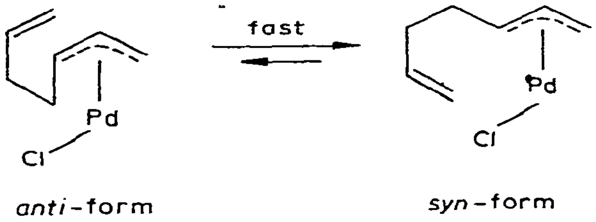


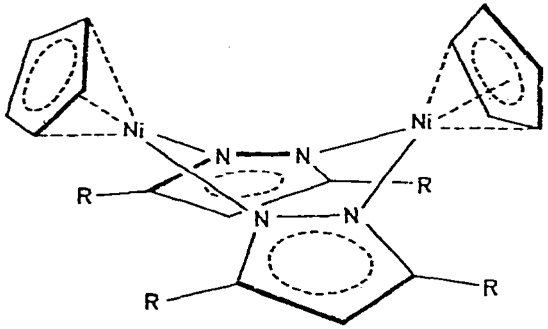
(149)

reaction of the π-allylpalladium compounds derived from some 3-oxo-4-ene steroids with malonate ion gives dialkyl (3-oxo-steroid-4-en-6β-yl) malonates in high yield, and with complete stereospecificity [227]. Triphenylstibine π-allyl palladium complexes have been prepared by cleavage of the halo bridge with $SbPh_3$ [228]. The oxidation of π-allylpalladium iodide by iodine in aqueous solution is unaffected by $[I^-]$ or by ionic strength. The activation enthalpy and entropy are 8.3 ± 1.0 kcal/mol and -30 ± 4 eu, respectively. A mechanism involving reversible substitution of I^- on Pd by I_3^-, followed by attack at the allyl by I^- is suggested. The products are PdI_4^{2-} and allyl iodide [229].

CNDO calculations for $Ni(\pi-C_3H_5)_2$ and $[NiX(C_3H_5)]_2$ (X = Cl, I) indicate the Ni-C bonds are more labile in the I than in the Cl, that the positive charge on Ni is lower in the I, and that the dimeric form is more stable in the I compound [230].

IX. Delocalized carbocyclic systems

Infrared evidence, including ^{13}CO data, are presented for the formation of [Ni(η-cp)CO], $[Ni(\eta-cp)(CO)_2]$, and ultimately $Ni(CO)_4$ on the UV photolysis of [Ni(η-cp)NO] in CO, or mixed CO and inert matrices, at 20 K [231]. $Ni(\eta-cp)_2$ reacts with 3,5-dialkylpyrazoles in benzene to give a red complex $[Ni(\eta^5-cp)(N_2C_3HR_2)]_2$ (R = Me, Et, i-Pr). The ^1H NMR spectrum is consistent with an equilibrium between the dimer and a paramagnetic monomer. The structure (150) is considered likely for the dimer [232]. A review of "triple" sandwich and "super" sandwich work has been published by Werner [233]. Treating $Ni(\eta^5-cp)_2$ with dimethyl phosphite gives $Ni(\eta^5-cp)[(MeO)_2PO]_2H$ (151). This compound can be deprotonated to give an anion which will act as a bidentate chelate ligand to cobalt or zinc (152) [234]. Thermally stable cationic carbonyl or monoolefin complexes of formulae $[M(\eta^5-cp)L(PR_3)]ClO_4$ (M = Ni, Pd, Pt; L = CO,



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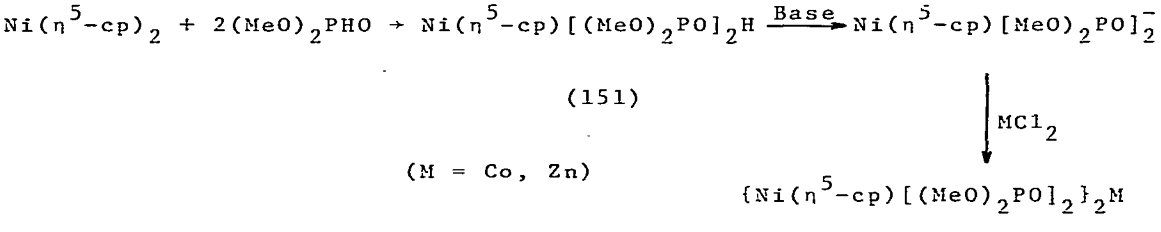
(150)

C_2H_4, C_3H_6; PR_3 = PPh_3, $PMePh_2$, $PPhMe_2$) have been isolated [235]. Dimeric palladium(I) complexes $[\mu\text{-}(\eta^3\text{-cp})\text{-}\mu\text{-}XPd_2(PR_3)_2]$ (153) (X = Br; R = *i*-Pr, Ph, Cy. X = Cl, I; R = *i*-Pr) have been prepared by



$$Ni(\eta^5\text{-cp})_2 + 2(MeO)_2PHO \rightarrow Ni(\eta^5\text{-cp})[(MeO)_2PO]_2H \xrightarrow{Base} Ni(\eta^5\text{-cp})[MeO)_2PO]_2^-$$

$$\downarrow MCl_2$$

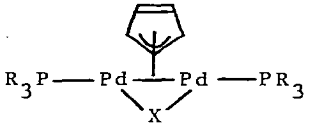
$$\{Ni(\eta^5\text{-cp})[(MeO)_2PO]_2\}_2M$$

(151)

(M = Co, Zn)

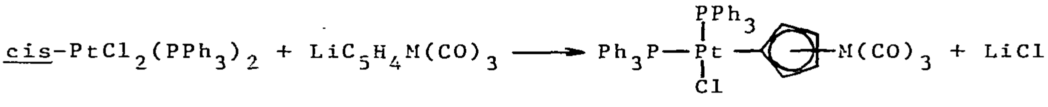
(152)

reduction of the complexes $[(\eta^5\text{-cp})PdX(PR_3)]$ with reducing agents such as Mg, Na/Hg, $LiAlH_4$ etc [236]. The crystal structure of the



(153)

complex $\mu\text{-cp-}\mu\text{-}BrPd_2[P(i\text{-}Pr)_3]_2$ shows the Pd and P atoms lying almost on a straight line with the two Pd atoms bonded together, and bridged by, the Br atom and by the cp ring. As suggested for (153), the ring can be considered as formed by an alkene group and an allyl group [237]. Treating *cis*-$PtCl_2(PPh_3)_2$ with $LiC_5H_4M(CO)_3$ (M = Mn, Re) gives the complex $PtCl(PPh_3)_2M(CO)_3(\eta^1\eta^5\text{-cp})$ (154) [238]. Similar



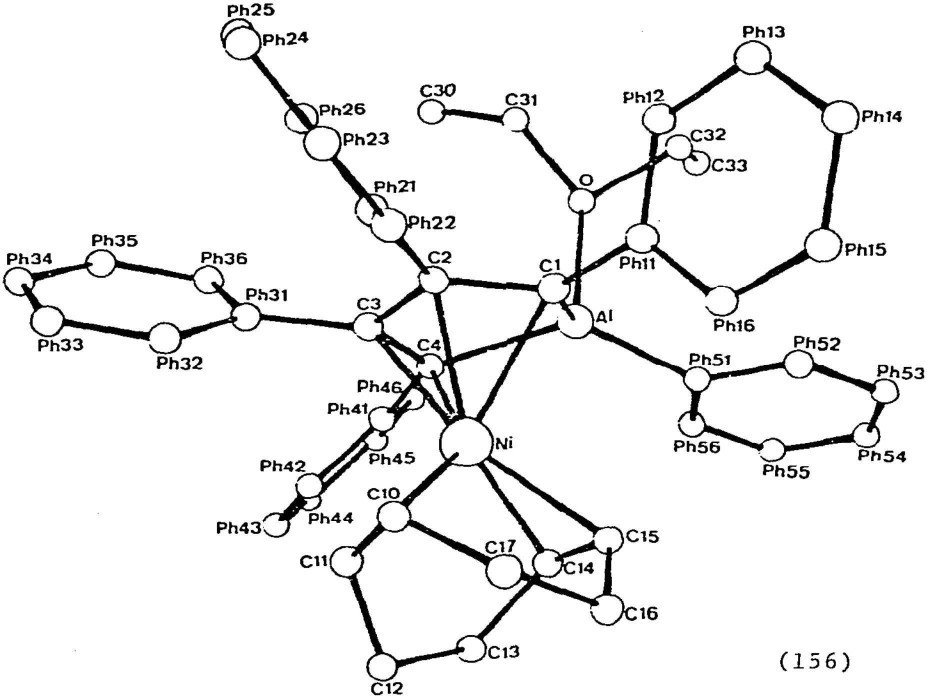
(154)

complexes have been obtained from $Pt(PPh_3)_3$ and $XHg(\eta^1\eta^5\text{-cp})M(CO)_3$ (M = Mn, Re; X = Cl, Br, I) [239]. The reaction of C_2RR^1 ($R = R^1 = CO_2H$, H, menthyloxycarbonyl; R = menthyloxycarbonyl, R^1 = Ph, CO_2H, H) with $Ni(\eta^5\text{-cp})_2$ gives both the complex $[Ni(\eta^5\text{-cp})]_2(C_2RR^1)$ (155), and the compound formed by Diels-Alder attack at the cp ring [240]. The molecular conformation of a complex (156) of (pentaphenyl)aluminacyclopentadiene with $Ni(1,5\text{-COD})_2$ shows a Ni-Al separation of

$$Ni(\eta^5\text{-cp})_2 + RC{\equiv}CR^1 \longrightarrow [Ni(\eta^5\text{-cp})]_2(RC{\equiv}CR^1)$$

(155)

2.748(1)Å [241]. Treating $PtCl_2(\eta^4\text{-}C_5HMe_5)$ with Br_2 yields



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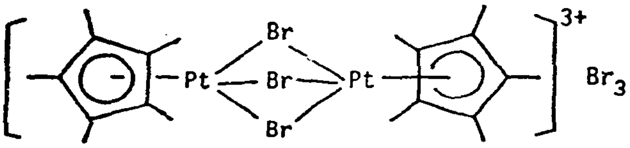
$[PtBr_3(C_5Me_5)]_n$ and structure (157) is suggested. The one-electron

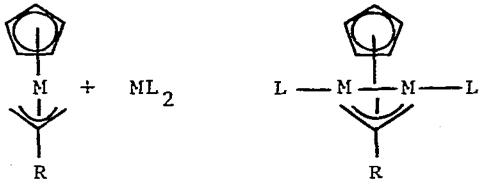


(157) [242]

reduction of nickelocene is abnormally slow, suggestive of a structural change [243]. The activation energy of nickelocene pyrolysis (340–420°) is 21.4 ± 0.2 kcal/mol. The major product is cyclopentadiene [244]. The negative ion mass spectrum of $Ni(acac)_2$ and 1,1'-bis($SiMe_3$)nickelocene has been recorded [245].

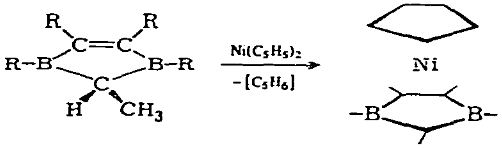
In reactions of the triple sandwich compound $[Ni_2(\eta\text{-cp})_3]BF_4$ with alkynes, it has been found that complexes $[Ni(\eta^5\text{-cp})_2]BF_4$ (158) and $[Ni(\eta\text{-cp})]_2(\eta\text{-RC}_2R^1)$ (159) are formed with alkynes C_2Ph_2, C_2HPh, $C_2(CO_2Me)_2$ [246]. Werner has also prepared complexes similar to (153) with a bridging cyclopentadienyl ligand. These complexes have been prepared from $M(\eta^5\text{-cp})(\eta^3\text{-allyl})$ and the reactive ML_2 (L = tertiary phosphine or phosphite) (M = Pd or Pt) species. The compounds have both a bridging allyl and a cyclopentadienyl (160) [247]. An unusual metallocycle (161) has been formed from $Ni(\eta^5\text{-cp})_2$ and substituted 1,3-diborolenes [248].

$$[Ni_2(\eta\text{-cp})_3]BF_4 + C_2RR^1 \longrightarrow \underset{(158)}{[Ni(\eta^5\text{-cp})_2]BF_4} + \underset{(159)}{[Ni(\eta\text{-cp})]_2(\eta\text{-RC}_2R^1)}$$



(M = Pd or Pt)

(160)



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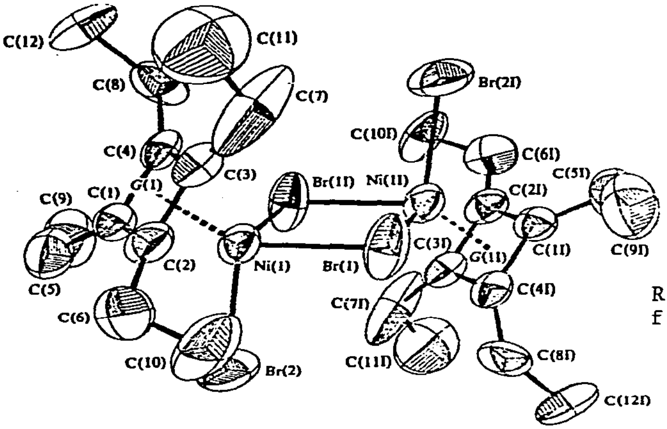
(161)

The structure of $[NiBr_2(C_4Et_4)]_2$ (162) shows equivalent C-C distances in the ring, which implies total electron delocalization [249]. At low temperatures the acetylene t-BuC≡CMe reacts with $PdCl_2(PhCN)_2$ to give a σ-butadienyl complex which rearranges to the cyclobutadienyl complexes $\{PdCl_2[C_4(\text{t-Bu})_2Me_2]_2\}$ or



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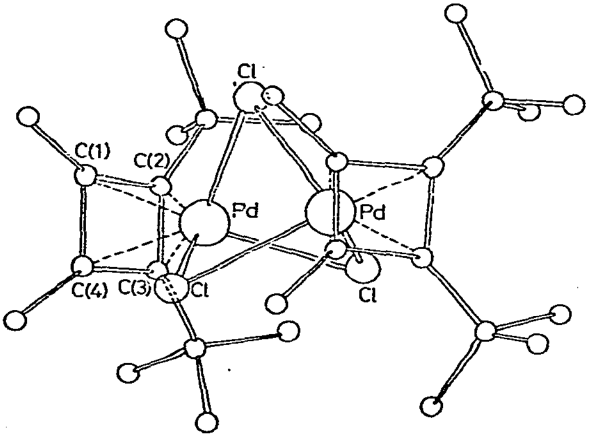
(162)

$\{Pd_2Cl_3[C_4(\underline{t}\text{-}Bu)_2Me_2]\}_2Pd_2Cl_6$ (163) [250]. The structure of the cation in (163) has been verified crystallographically. Addition



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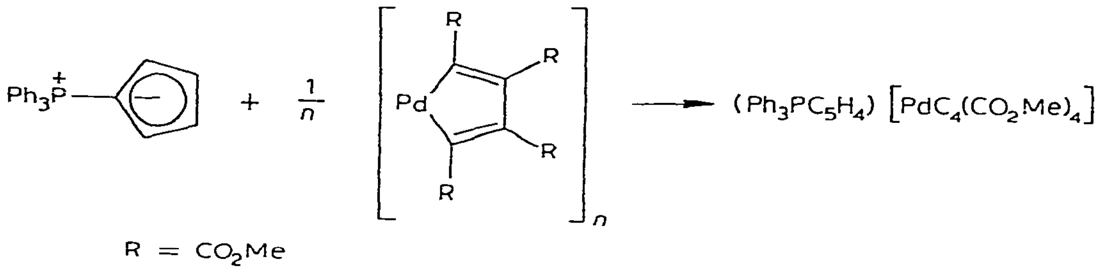
(163)

of the triphenylphosphonium cyclopentadienylylide to tetrakis(methoxycarbonyl)palladiacyclopentadiene yields the monomeric complex (cpylid) $[PdC_4(CO_2Me)_4]$ (164). The NMR spectra of the cp ring protons indicate unsymmetrical ring coordination [251]. The structure shows that intramolecular separations between phosphonium phenyl rings and palladiacycle methyl carboxylate groups restrict the Pd to the lower region of the ylide. Acting as a cyclic diene, (pentaphenyl) aluminacyclopentadiene forms olefin complexes with nickel with elimination of the aluminum, and the isolation of a tetraphenylcyclobutadiene complex (165) [252]. Phenylation of $PdCl_2(\eta^4$-norbornadiene) with $HgPh_2$ or $NaBPh_4$ gives di-μ-chlorobis(2:5,6-η-3-endo-



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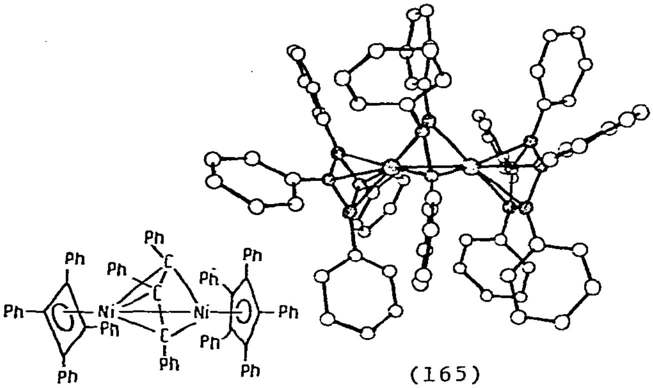
phenylnorbornen-2-yl-endo)Pd. This reaction provides the first definitive evidence for a *cis* addition of Pd–R to a coordinated double bond. The complex undergoes a reversible ring-closure to give the nortricyclenyl complex on reaction with pyridine. Phenylation of $PtCl_2(\eta^4$-norbornadiene) gives first PtCl(Ph)(nor-C_7H_8), and then $PtPh_2$(nor-C_7H_8), and no phenylation can be induced [253].



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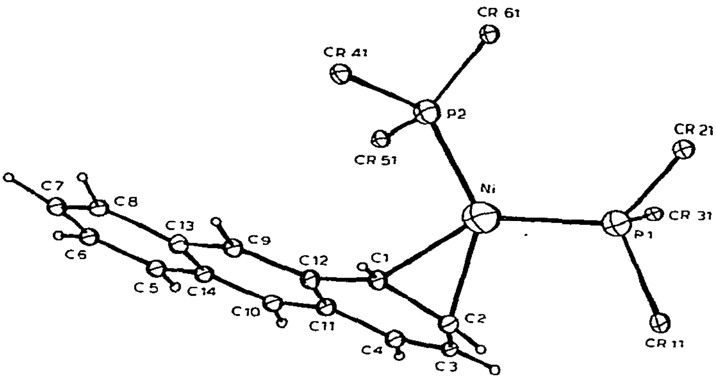
The complex $[Ni(fulvalene)_2]_2$ has been prepared from $Ni(acac)_2$ and the fulvalene dianion. The complex will undergo electron transfer, and the compound has been obtained in 3 oxidation levels [254]. The structure of $Ni(1,2\text{-}\eta^2\text{-anthracene})(PCy_3)_2$ (166) shows a lengthening of the coordinated C–C bond of anthracene by 0.047(6)Å. The substitution planes at these carbons are bent back 19(1)° from the Ni atom [255]. The tetrameric complex $[Ni_2(CO)_2(\mu_2\text{-}C_3Cl_3)(\mu_2\text{-}Cl)]_2$ (167) has been prepared from $Ni(CO)_4$ and C_3Cl_4 [256]. The structure consists of a 6-membered Ni_4Cl_2 ring which is planar. The C_3Cl_3 ring-opened species is planar and is orthogonal to the Ni_4Cl_2 plane. Treating $Ni(\pi\text{-}C_3H_5)_2$ with quinones L (L = duroquinone, tetramethoxy-*p*-benzoquinone, 9,10-anthraquinone, tetraphenylcyclopentadienone)



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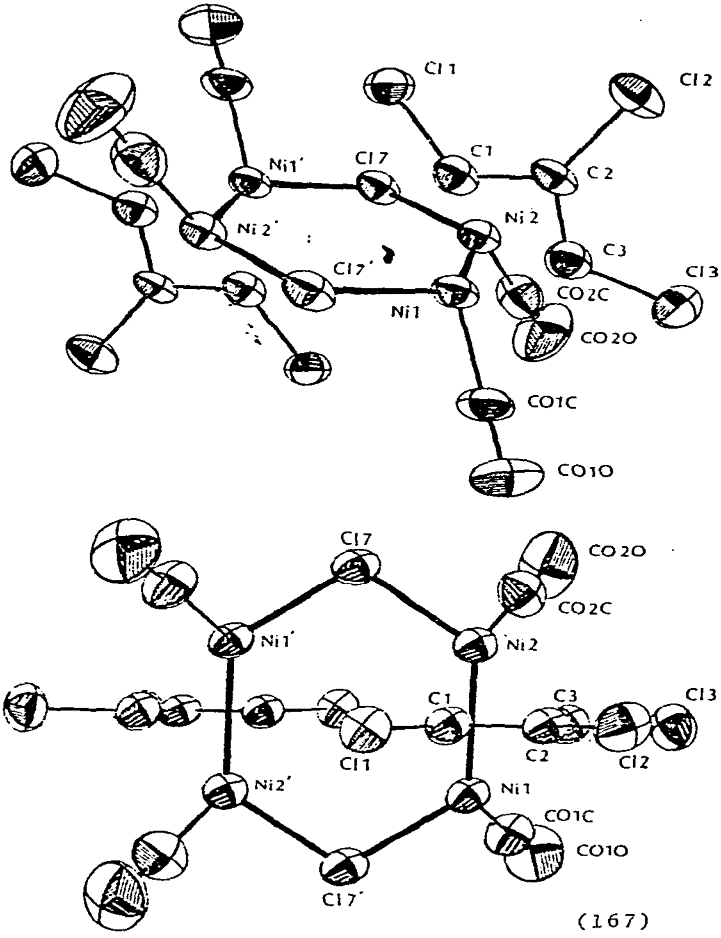
(166)

gives good yields of Ni(π-C_3H_5)$_2$L [257]. The structure of Pt(2,3-η(1,4-benzoquinone)(PPh_3)$_2$ (168) shows the benzoquinone bonded as



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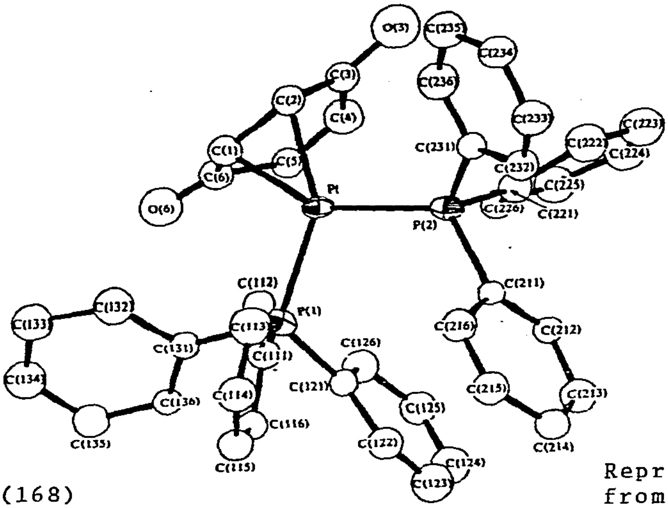

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a mono-olefinic ligand to Pt. The quinone ring adopts an irregular boat conformation, and other distances and angles are discussed [258].

X. Metal hydrides

In an article describing the chemistry of $NiEt(acac)PPh_3$ it has been found that reaction with Et_2AlBr gives the new nickel hydride compound $Ni(H)Br(PPh_3)_3$ (169). The compound has also been prepared directly from $Ni(acac)_2$. The structure of $[NiH(Cy_2PCH_2CH_2CH_2PCy_2)]_2$

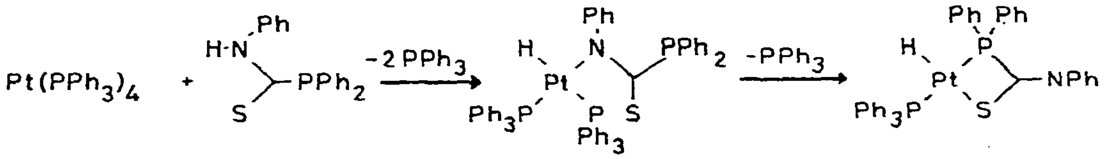
$$NiEt(acac)PPh_3 + Et_2AlBr + 2PPh_3 \longrightarrow Ni(H)Br(PPh_3)_3 + C_2H_4 + C_2H_6$$

$$Ni(acac)_2 + Et_2AlBr + 3PPh_3 \longrightarrow Ni(H)Br(PPh_3)_3$$

(169)

has the nickel atoms doubly bridged by hydrogens. The Ni-Ni and average Ni-H distances are 2.441 and 1.6Å respectively. Theoretical considerations predict a square-planar structure for the idealized molecule with a soft potential energy surface for a twisting motion towards the observed geometry [260]. The intermediate $PdH_2(PPh_3)_2$ has been proposed in the β-elimination reaction induced from a mixture of $PdCl_2(PPh_3)_2$ and $LiNMe_2$ [261]. The compound $Pd(H)Cl[OP(OEt)_2]_2H$ has been prepared by the $NaBH_4$ reduction of $\{Pd(\mu-Cl)[OP(OEt)_2]_2H\}_2$ obtained from $(EtO)_2POH$ and $[PdCl(allyl)]_2$. The compound is likely an anion rather than Pd(III). The hydride complex has been used to catalyze the hydrogenation alkynes to alkenes and nitrobenzene to aniline [262].

The preparation and IR and NMR spectra of 123 platinum hydrides of formulae trans-$PtHX(PBz_3)_2$ and trans-$[PtHL(PBz_3)_2]BPh_4$ (Bz = benzyl) are described [263]. Trends in ν(PtH), τ(PtH), ^1J(PtH) and ^1J(PtP) are discussed. Sodium borohydride has been used to prepare PtH(t-$Bu_2PCH_2CO_2$){t-$Bu_2P(CH_2)_2OH$} [264]. The compound $Pt(PPh_3)_4$ reacts with $Me_2NC(S)N(H)C(S)NMe_2$ and $HN(Ph)C(S)PPh_2$ to give $PtH[Me_2NC(S)NC(S)NMe_2]PPh_3$ and $PtH[Ph_2PC(S)NPh]PPh_3$ (170) respectively [265]. The compounds are formed by N-H addition. When the complex trans-$PtH(CH_2CH_2CH_2CN)(PPh_3)_2$ is treated with an excess of RNC



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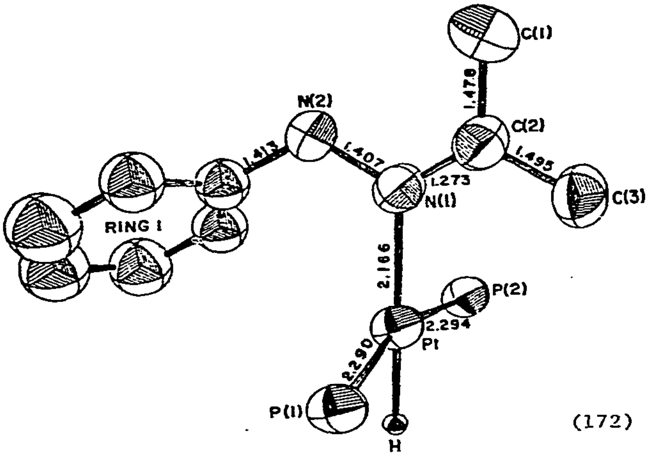
(R = t-Bu, 2,6-$Me_2C_6H_4$) the product is $Pt(CNR)_2(PPh_3)_2$. With trans-$PtH(CH_2CN)(PPh_3)_2$, however, the complex formed is $PtH(CH_2CN)CNR(PPh_3)$ [266]. The preparation and spectroscopic properties of cis and trans-$PtH(CH_2CN)(PPh_3)_2$ and $PtH(CH_2CN)(L-L)$ (L-L = dpe, dpp etc) are described [267]. The hydrido-1,3-di-p-triazenido complex of platinum(II), trans-$PtH(p\text{-}MeC_6H_4N\text{-}N{=}NC_6H_4Me\text{-}p)(PPh_3)_2$ reacts with CO, 2,6-$Me_2C_6H_3NC$, PPh_3, and PhC≡CPh under mild conditions to yield Pt(0) complexes by reductive elimination of 1,3-di-p-tolyltriazene [268]. The mechanism of the reaction is considered with respect to the formation of a pentacoordinate intermediate [268].

$$PtH(ArN_3Ar)(PPh_3)_2 \begin{cases} \xrightarrow{RNC} Pt(CNR)_2(PPh_3)_2 \\ \xrightarrow{PHC\equiv CPh} Pt(PhC\equiv CPh)(PPh_3)_2 \end{cases}$$

The complex $Pt(BF_4)(NNAr)(PPh_3)_2$ can be hydrogenated in ethanol to give the hydrazine complex (171), which dehydrates to the hydrazone complex (172) [269]. The structure of the hydrazone complex (172)

$$Pt(BF_4)(NNAr)(PPh_3)_2 \xrightarrow[EtOH]{H_2} \underset{(171)}{[PtH(H_2NNHAr)(PPh_3)_2]BF_4} \xrightarrow{-H_2O} \underset{(172)}{[PtH(ArHNNC_3H_6)(PPh_3)_2]BF_4}$$



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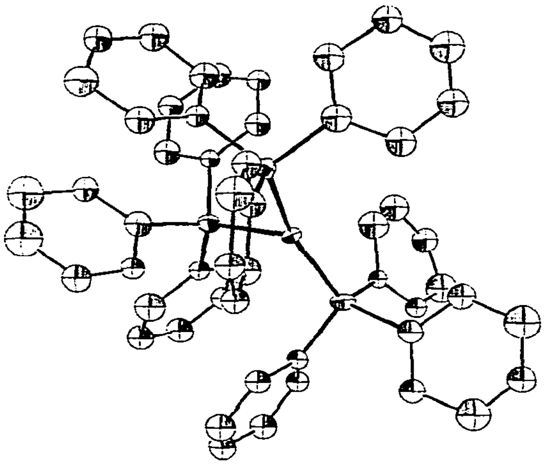
has been solved. Organoboron adducts of the type *trans*-$PtHL_2NC{\cdot}BR_3$ (L = PEt_3) rapidly isomerize to the thermodynamically stable isomer *trans*-$PtHL_2CN{\cdot}BR_3$. The activation energy is related to the strength of the Lewis acid, and is catalyzed by triarylboron compounds [270]. From reactions of *trans*-$PtH_2(PCy_3)_2$ with CO_2, the complexes *trans*-$PtH(O_2CH)(PCy_3)_2$ and *trans*-$PtH(O_2COMe)(PCy_3)_2$ have been obtained. Both compounds have been verified by X-ray crystallographic techniques [271]. The crystal structure of the complex $[PtH(PPh_3)_3](CF_3CO_2)_2H$ (173), obtained from $Pt(PPh_3)_3$ and CF_3CO_2H, shows a planar geometry about platinum(II), with the angle P-Pt-P of approximately 99° [272]. The complex *trans*-$PtH(CF_3)(PPh_3)_2$ (174)



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has been prepared by treating $PtX(CF_3)(PPh_3)_2$ with $NaBH_4$ in ethanol. Among other reactions, the complex reacts with isocyanides CNR to

$$trans\text{-}PtX(CF_3)(PPh_3)_2 \xrightarrow{NaBH_4} trans\text{-}PtH(CF_3)(PPh_3)_2 \qquad (174)$$

give complexes trans-$PtH(CNR)(PPh_3)_2$ [273]. A series of interesting platinum(II) hydrides have been obtained by the oxidative addition of HX to the compound $Pt(PCy_3)_2$ [274]. Among the complexes reported are: $PtH_2(PCy_3)_2$, $PtH(R)(PCy_3)_2$ (R = C_6F_5, 1,3,5-$C_6F_3H_2$, 1,3-$C_6F_2H_3$, C_6F_5O, PhO, C_6F_5NH, C_4H_4N), $PtH(C_6F_5)(PEt_3)_2$. The complex $[Pt(SiR_3)(\mu\text{-}H)PCy_3]_2$ has been found to catalyze the addition of silanes R_3SiH (R = Me, Et, CH_2Ph, Ph, OEt, Cl) to pentene-1, hexene-1, styrene, allyl chloride, and 2-methylpropene. Reactivity orders are given. The addition of Me_3GeH to hexene-1 is catalyzed by $[Pt(GeMe_3)(\mu\text{-}H)PCy_3]_2$ [275]. In the following paper these hydrides are used as catalysts for the hydrosilylation of alkynes [276].

When two equivalents of trans-$PtHCl(PEt_3)_2$ are treated with one equivalent of Me_3SiPH_2, the complex trans-$[PtH(PEt_3)_2]_2PH_2^+Cl^-$ (175) is formed. This compound reacts with HCl to give either the fully (176) or partially oxidized compound, depending on the quality of HCl used [277]. New hydrides $[Pt_2H_3(L\text{-}L)_2]BF_4$ ((L-L) = dpe, $Ph_2AsCH_2CH_2AsPh_2$) have been obtained by the reaction of [Pt(3,5-dimethylpyrazole)(L-L)]$(BF_4)_2$ (177) with KBH_4 in MeOH or EtOH as

$$2\ \underline{\text{trans}}\text{-}PtHCl(PEt_3)_2 + Me_3SiPH_2 \xrightarrow[-Me_3SiCl]{} \underline{\text{trans}}\text{-}[PtH(PEt_3)_2]_2PH_2^+Cl^-$$

(175)

$$\xrightarrow{HCl} [(PEt_3)_2ClH_2Pt\text{-}PH_2\text{-}PtH_2Cl(PEt_3)_2]^+$$

(176)

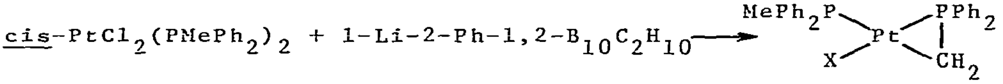
solvent [278]. A bridging hydride has been obtained by treating $[PtCl(dpm)]_2$ with sodium borohydride or with HCl. In the former case the product is $[Pt_2H_2(\mu\text{-}H)(dpm)_2]Cl$, and in the latter case the complex $[Pt_2Cl_2(\mu\text{-}H)(dpm)_2]Cl$ is formed. In the sequence of reactions reported, the complex $[Pt_2H_2(\mu\text{-}Cl)(dpm)_2]Cl$, along with the PF_6 salts, have been isolated [279].

$$[Pt(3,5\text{-dimethylpyrazole})L\text{-}L](BF_4)_2 + KBH_4 \longrightarrow [Pt_2H_3(L\text{-}L)]BF_4 + 3,5\text{-dimethylpyrazole}$$

(177)

XI. Metal carboranes

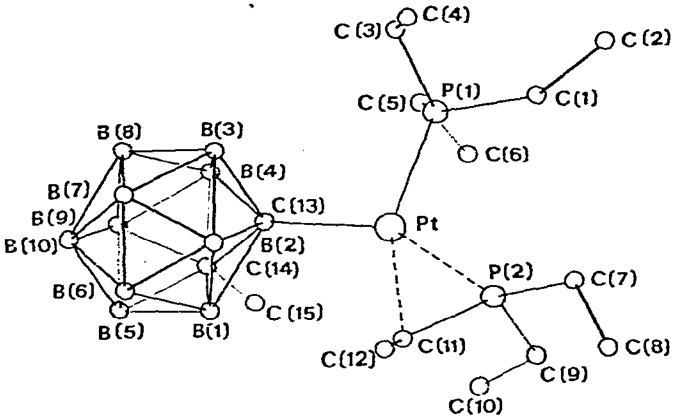
The complexes $Ni(1,2-B_9C_2H_{11})_2$ and $Ni(1,7-B_9C_2H_{11})_2$ have been thermolyzed at 210-220°C in *vacuo*. One direction for reaction is the formation of $C_2B_7H_9$ and $C_2B_9H_{11}$ which undergo subsequent pyrolysis. For the complex $Ni(1,2-B_9C_2H_{11})_2$, thermal isomerization into a mixture of isomers occurs [280]. The reaction of $NiCl_2$(dpe) with $Me_4C_4B_8H_8^{2-}$ produces two isomers of the 12-vertex system $Ni[Me_4C_4B_7H_7]$dpe, and three isomers of the 13-vertex system $Ni[Me_4C_4B_8H_8]$dpe [281]. Prolonged treatment of *cis*-$PtCl_2(PMePh_2)_2$ with a large excess of $1-Li-2-Ph-1,2-B_{10}C_2H_{10}$ in ether produces the internally metalated complex *cis*-1-[$(MePh_2P)Pt(PCH_2Ph_2)$]-2-Ph-1,2-(σ-$B_{10}C_2H_{10}$) (178) in which a methyl group of one coordinated phosphine is involved in the ring formation [282]. The structure of Pt[2-methyl-1,2-dicarbabadodecaboranyl(10)](triethylphosphine)(diethylethylidenephosphine) (179) shows the 2-methyl-1,2-carboranyl group σ-bonded to Pt through its 1 C atom. One phosphine is coordinated to the metal atom through its P atom, and the other through both its P atom and the first C atom of one ethyl side group [283]. The structure of the complex *nido*-3,8-dimethyl-2,2-bis(triethylphosphine)-3,8-dicarba-2-platinanonaborane(6) (180) has a 9-atom



$$cis\text{-}PtCl_2(PMePh_2)_2 + 1\text{-}Li\text{-}2\text{-}Ph\text{-}1,2\text{-}B_{10}C_2H_{10} \longrightarrow$$

+ LiCl + HCl

$(X = 2-Ph-1,2-B_{10}C_2H_{10})$ (178)



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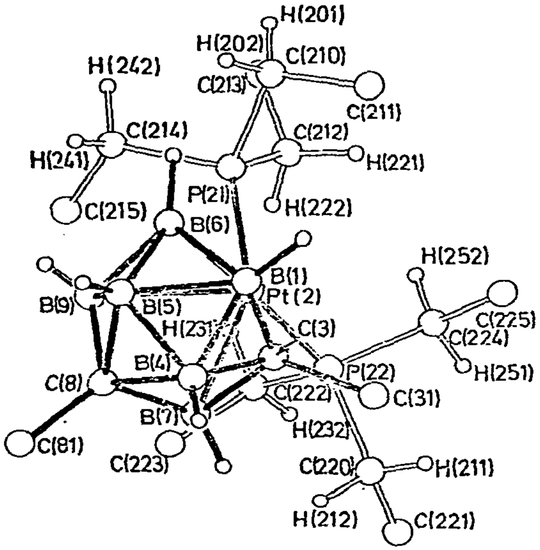
metallacage based on a tricapped trigonal prism in which the metal lies in a prism face, adjacent to B and C caps [284]. Extended



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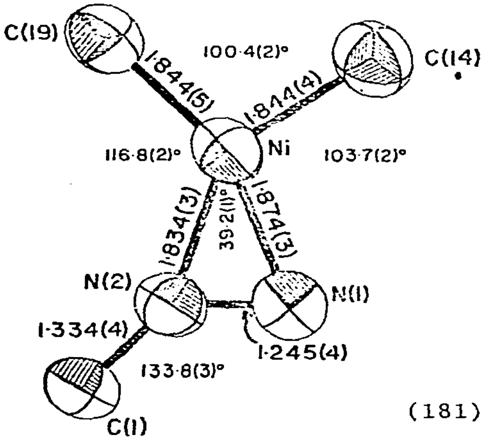
Hückel calculations on model borane complexes account for the magnitude and direction of the slipped distortions when substituents on the open pentagonal face of the ligands are changed in complexes $L_2MC_nB_{11-n}$ (L = PR_3, RNC; M = Pd, Pt; n = 1,2) [285].

XII. Metal isocyanides

Diazofluorene reacts with complexes M(t-BuNC)$_2$ or M(C_2H_4)(PPh_3)$_2$ (M = Ni, Pd) to give complexes ML_2(diazofluorene). The structure of Ni(t-BuNC)$_2$(diazofluorene) shows the diazofluorene molecule π-bonded to Ni through the N–N multiple bond (181). A correlation is



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noted between Ni-C distances, the ν(C≡N) values, the C-Ni-C angles of the t-BuNC ligands, and the π-acidity of the ligand AB in complexes $Ni(t\text{-}BuNC)_2AB$ [286]. A series of complexes of nickel(0) have been prepared with π-carboxo ligands. These complexes are of the type $Ni(\pi\text{-}O{=}CR_1R_2)(t\text{-}BuNC)_2$ and have a range of substituents for R of CN, CO_2R, CF_3, F, $CF{=}CF_2$ [287]. A linear correlation is found when $\nu^1(NC)$ for these complexes is plotted against $\nu^1(NC)$ for a similar series of π-olefin nickel complexes.

Reaction of alkyl isocyanides with $Ni(1,5\text{-}COD)_2$ gives the nickel cluster compound $Ni_4(CNR)_x$ with the four Ni atoms describing the vertices of a highly compressed tetrahedron [288]. The complex $Ni_4(CNCMe_3)_7$ is stereochemically nonrigid, and will catalyze the trimerization of acetylenes to benzenes, butadiene to 1,5-COD, the polymerization of allene, and the selective hydrogenation of acetylenes to *cis* olefins. In a further article, it is reported that the complex $Ni_4(CNCMe_3)_7$ can be used as a catalyst for the selective hydrogenation of both an isocyanide and acetonitrile [289]. From Me_3CNC the products obtained are Me_3CNHMe and Me_3CNH_2. The hydrogenation of acetonitrile to ethylamine at 90°C was carried out homogeneously in the presence of $Ni_4(CNCMe_3)_7$

When $PdCl_2(1,5\text{-}COD)$ is treated with triphenyl(phenylimino)phosphorane and CO, the product is a mixture of the isocyanide (182) and

$$\begin{tikzcd}
PdCl_2(1,5\text{-}COD) + 2\,PhN{=}PPh_3 + CO \arrow[r, "-Ph_3PO"'] & PdCl_2(PhN{=}PPh_3)(CNPh) \arrow[d, "CO"] \\
& PdCl_2(PhN{=}PPh_3)CO
\end{tikzcd}$$

(182)

(183)

carbonyl (183) complexes [290]. The dimeric complexes $[PdCl_2(CNAr)]_2$ (Ar = *p*-anisyl, *p*-tolyl) react with *o*- and *p*-substituted primary and secondary anilines NHRAr' (R = H, Me, Et; Ar' = Ph, *p*-tol, *p*-ClC_6H_4, *o*-tol) [291]. The reaction involves an initial fast halide-bridge splitting to form *trans*-$PdCl_2(CNAr)(NHRAr')$, followed by a reaction of a second molecule of amine with the coordinated isocyanide to give the carbene derivatives *trans*-$[PdCl_2\{C(NHAr)NRAr'\}(NHRAr')]$. This latter stage occurs stepwise *via* direct nucleophilic attack on the isocyanide carbon, followed by proton transfer to the final carbene complex. The rates of carbene formation depend on the steric and electronic characteristics of both metal complex and amine. Solid-phase thermolysis of $[Pt(CNR)_4][PtX_4]$ (R = Cy; X = Cl, Br, I) gives *cis*-$PtX_2(CNR)_2$ (X = Cl, Br) and *trans*-$PtI_2(CNR)_2$. The *trans* effect of CNR is considered to be greater than that of Cl^- and Br^-, but less than that of I^- [292].

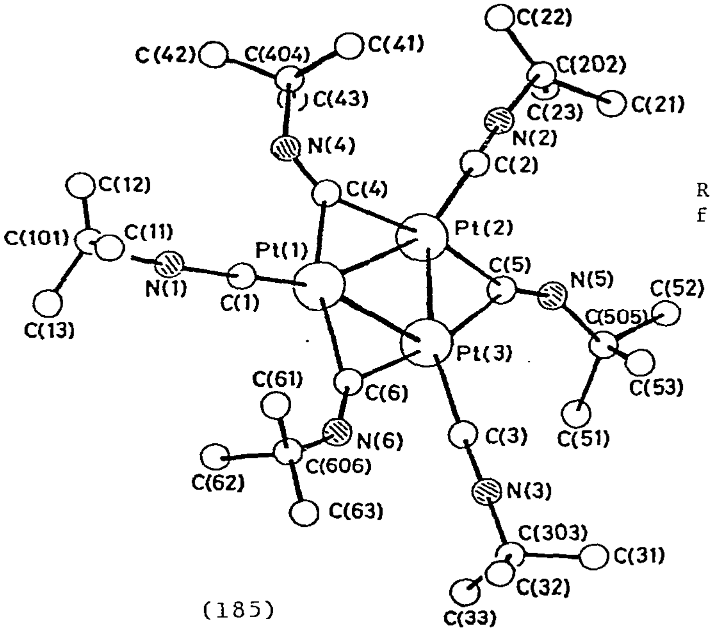
Substitution reactions of $[Pd_2(CNMe)_6](PF_6)_2$, $[Pt_2(CNMe)_6](BF_4)_2$, and $[PdPt(CNMe)_6]PF_6$ have been studied [293]. Exchange with free MeNC is fast, and MeNC can be replaced by *t*-BuNC. For the reaction with PPh_3, axial substitution is preferred. The fluxional behavior of $[Pd_2(CNMe)_6]^{2+}$ and $[Pd_2(CNMe)_5PPh_3]^{2+}$ has been investigated by ^1H NMR line-shape techniques.

The species isodiazomethane has been stabilized by coordination. The complex (184) has been prepared by suspending solid PdI_2 in an ether solution of isodiazomethane at -10°C [294].

$$H_2CN_2 \xrightarrow[(ii)\,H_2O]{(i)\,LiMe} CNNH_2 \xrightarrow[Et_2O]{PdI_2} PdI_2(-C{\equiv}NNH_2)_2\cdot 2Et_2O$$

(184)

A series of cationic isocyanide complexes of Pd and Pt of the type $[MCl(p\text{-}MeC_6H_4NC)L_2]ClO_4$ (M = Pd, Pt; L = $P(p\text{-}tol)_3$, $P(o\text{-}tol)_3$, PCy_3, $AsMePh_2$, $AsEtPh_2$, $AsPrPh_2$, $AsCy_3$) have been prepared. The values for ν(CN) are in the region of 2200 cm^{-1} as compared to



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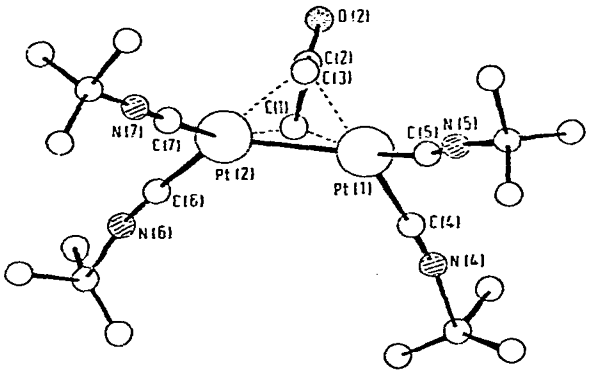
2130 cm^{-1} for free ligand, suggestive of weak π-character in the M-C bond [295]. Treating Pt(1,5-COD)$_2$ with t-BuNC gives a quantitative yield of Pt_3(t-BuNC)$_6$. Similar complexes with MeNC, EtNC and CyNC can be obtained. The structure of Pt_3(t-BuNC)$_6$ shows an equilateral triangle of Pt atoms, each having a terminal isocyanide ligand. The remaining three t-BuNC groups bridge the sides of the triangle (185) [296]. The ^1H and ^{13}C NMR spectra show intermolecular dynamic behavior involving terminal and bridge isocyanide site exchange catalyzed by free ligand. In the following paper, these workers describe and discuss the chemistry of Pt_3(t-BuNC)$_6$ with $(CF_3)_2CO$, C_2H_4, $CF_3CF{=}CF_2$, $CF_3CF{=}CFCF_3$, and $(CN)_2C{=}C(CF_3)_2$ [297]. Cyclic products are formed in many cases. When Pt_3(t-BuNC)$_6$ is treated with diphenylcyclopropenone, a complex $[Pt_2\{\mu_2\text{-}(PhC)_2CO\}(t\text{-}BuNC)_4]$ (186) is formed. The structure of (186) shows a ring-opened C_3 fragment perpendicular to the line of the Pt atoms [298].



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XIII. Catalytic reactions involving complexes

The diene 1,3-COD has been selectively hydrogenated to cyclooctene in a homogeneous reaction with a catalyst prepared from H_2PtCl_6-$SnCl_2\cdot 2H_2O$ along with the additives HBr and H_2O, in iso-propanol solvent [299]. Unsaturated compounds have also been homogeneously hydrogenated by a catalyst prepared from $NiCl_2\cdot 6H_2O$ in DMF or DMA solvent. The catalytic solution is very sensitive to traces of air [300]. The platinum mixture has also been used by these authors as a catalyst for the homogeneous hydrogenation of unsaturated esters with turnover numbers of greater than 1600 [301]. Cyclohexene has been hydrogenated using halo-transition metal complexes supported on phosphine-modified silica carriers. The complexes used in the nickel triad are derived from $NiCl_2$, $NiBr_2$ and $PdCl_2$.

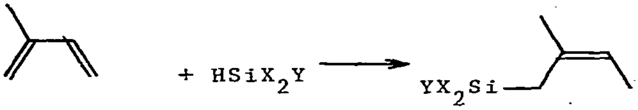
The complexes are 2 to 4 orders of magnitude more active than their homogeneous counterparts [302]. The catalytic hydrogenation of styrene in the presence of a $PdCl_4^{2-}$ catalyst has been studied by an all-valence-electron SCF method [303]. A palladium hydride with a dioxaphosphorinane ligand has been formed which is an effective hydrogenation catalyst for alkynes and dienes. The activity of the complex is dependent on whether the palladium is coordinated to phosphorus in an axial or equatorial position [304].

The hydrosilylation of olefins $RC_6H_4CH{=}CH_2$ (R = H, Cl, OMe) and 1-octene with alkylchlorosilanes in the presence of $Ni(\eta^5\text{-cp})_2$ proceeds to give α-adducts as per Markovnikov's rule. The rate of addition follows the sequence $HSiCl_3 > HSiMeCl_2 > HSiMe_2Cl > HSiMeEt_2$ [305]. Rate constants and activation parameters have been determined for the hydrosilylation of $CH_2{=}CHR$ (R = CH_2CN, C_6H_4Cl, Ph, CH_2Ph, Bu, pentyl), p-$CH_2{=}CMeC_6H_4Me$, and $CH_2{=}CMe(CH_2)_3CHMe_2$ by Me_2SiHPh in the presence of a platinum-containing anion exchanger. The main factor governing formation of the active Pt-silane-olefin complex is entropy [306]. Kinetic data for the hydrosilylation of p-$RC_6H_4CH{=}CH_2$ (R = Me, H, Cl) by Me_nSiHCl_{3-n} (n = 0-3) with $K[PtCl_3(C_2H_4)]$ or H_2PtCl_6 as catalyst indicates that the reaction proceeds in the coordination sphere of pentacoordinate complexes of Pt(II) without preliminary cleavage of Si-H and C=C bonds [307]. A pentacoordinate intermediate has also been suggested for the addition of $MeSiHCl_2$ to p-$RC_6H_4CH{=}CH_2$ (R = H, MeO, Cl) in the presence of PPh_3-Pt complexes. Differences were observed between cis- and trans-complexes [308]. The hydrosilylation of conjugated dienes with Me_2SiH_2 can be carried out using a catalyst composed of $Ni(acac)_2$, Et_3Al and PPh_3 [309]. Deuteriosilylation of 1,3-butadiene, isoprene and 3-methyl-1,4,6-pentatriene with Me_3SiD in the presence of this same Ni composition gives deuterated products; the ratios are given [310]. The hydrosilylation of isocyanates is promoted by Pd catalysts and gives N-silylformamides (187) or C-silylamides (188). The catalysts used are Pd/C or $PdCl_2$ [311]. The hydrosilylation of isoprene

$$R\text{-}N{=}C{=}S + Et_3SiH \longrightarrow RN(SiEt_3)CHO \text{ or } RNH(CO)SiEt_3$$

(187, R = aryl) (188, R = alkyl)

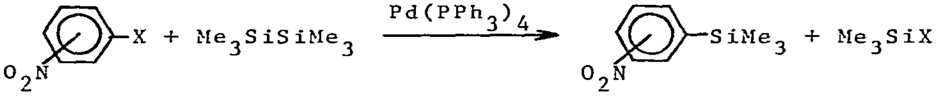
catalyzed by a palladium catalyst prepared in situ from $PdCl_2(PhCN)_2$ and PPh_3 proceeds regioselectively and stereoselectively to give (Z)-2-methyl-buten-2-ylsilane (189) exclusively. A mechanism is proposed [312]. The hydrosilylation of cyclohexadienes using



(X=Y=Cl; X=Cl, Y=Me; X=Me, Y=Cl) (189)

$Na(acac)_2/Al(OEt)Et_2$ gives only the allylic cyclohexenylsilane with both 1,3- or 1,4- (in presence of a phosphine) cyclohexadienes. 2,3-Dimethyl-1,3-butadiene gives mainly the product of 1,4- rather than 1,2-addition, but the proportion of the latter is increased by adding PPh_3 into the catalyst [313]. o-, m-, and p-Nitrophenyltrimethylsilanes and 2,4-dinitrophenyltrimethylsilane have been prepared from the reactions of hexamethyldisilane with the corresponding nitrohalobenzenes catalyzed by $Pd(PPh_3)_4$ [314].

A mixture of $Ni[CH(COMe)_2]_2$, L (L = $P(OPh)_3$, $P(OEt)_3$, PBu_3, $SbPh_3$), Et_3Al, and NaOH in a 1:1:2:1 ratio catalyzes the addition



of MeOH to methyl acrylate, maleate and fumarate [315]. The dimerization of a deuterium labelled butadiene with a $Ni(1,5\text{-}COD)/PPh_3$ catalyst shows a mechanism with both diene units isomerized at both termini. The involvement of σ-allyls is supported [316]. Complexes of Ni(0) and Ni(II) have been used to trimerize acetylenes $RC{\equiv}CNR'_2$ to benzenes. The compounds formed have the dialkylamino substituent at the 1,2,4-positions [317]. A 1,3-diene is formed on the catalyzed addition of phenylacetylene to styrene. The catalyst used is a mixture of $PdCl_2$ and LiCl under an oxygen atmosphere [318]. Olefins can be cotrimerized with a phosphinated polystyrene resin-anchored $PdCl_2$-$AgBF_4$ mixture [319]. Kinetic data has suggested that the rate-determining step in the dimerization of styrene to PhCH=CHCH=CHPh with $Pd_3(OAc)_6$ is the reaction of styrene with the trimer. With $Na_2Pd(OAc)_4$ the rate is immeasurably slow [320]. The dimerization of propene is catalyzed by $Ni[P(OC_6H_4R\text{-}o)_3]_2$ (R = Me, OMe), $Ni(PPh_3)_4$, $Ni[P(OEt)_3]_4$ or $Ni(C_2H_4)(PPh_3)_2$ in the presence of CF_3CO_2H or H_2SO_4 [321]. Nickel hydrides are involved. The reaction of biacetyl with $Ni(1,5\text{-}COD)_2$ proceeds catalytically to give oligomers of biacetyl. Use of the complex $Ni[P(OPh)_3]_4$, which has a strongly coordinated ligand, suppresses the reaction with biacetyl [322]. Nickel bromide and mesitylmagnesium bromide react with 3-hexyne under nitrogen between -40° and 68°. At the lower temperature a partially ordered unsaturated linear polymer of the acetylene and hexaethylbenzene are formed, but at the higher temperature only catalytic cyclotrimerization occurs [323].

The mixture of $PdCl_2$ and sodium acetate catalyzes the homogeneous oxidation of secondary alcohols to ketones by O_2 at room temperature. Negligible ketone is formed in the absence of acetate [324]. A kinetic and mechanistic study has been published on the catalytic oxidation of triphenylphosphine with $Pt(PPh_3)_3$. Use of substrates $PMePh_2$

$$R^1R^2CHOH + 1/2\ O_2 \longrightarrow R^1R^2C{=}O + H_2O$$

and $PPhMe_2$ has shown that the mechanism involves formation of the hydroperoxide ion (HO_2^-), which acts as an oxidant to the phosphine. Interestingly this mechanism does not involve direct oxygen transfer from the metal dioxygen complex to the substrate, and such a pathway

$$Pt(PPh_3)_2O_2 + 4\ PPhMe_2 + EtOH \longrightarrow Pt(PPhMe_2)_4^{2+} + 2\ PPh_3 + HO_2^- + EtO^-$$

$$HO_2^- + PPhMe_2 \longrightarrow Me_2PhPO + OH^-$$

as the one found is only to be anticipated when a strong nucleophile such as a phosphine is a substrate. This conclusion is reached since the phosphine is involved in displacement of the coordinated peroxide from the metal [325]. The kinetics of the catalytic liquid phase oxidation of CO by oxygen have been studied in the presence of triphenylphosphine-palladium complexes using $^{18}O_2$ and $H_2{}^{18}O$. Analysis of the oxidation products shows that the oxidation involves reduction of palladium(II) to $Pd(PPh_3)_4$ in acidic solutions, and to triphenylphosphine-PdO_2 complexes in neutral solution [326]. Ketones can be oxidized to carboxylic acids using the complex $Pt(PPh_3)_3$ as

$$RCH_2COR + O_2 \longrightarrow 2\ RCO_2H$$

catalyst. Methyl ketones are not oxidized, and carbon monoxide is not oxidized to carbon dioxide. The reaction involves a free-radical autoxidation pathway [327]. Treatment of cyclohexyl hydroperoxide in CCl_4 with an aqueous solution containing Na_2PdCl_4 and $FeSO_4$ gives $Me(CH_2)_2CH{=}CHCHO$ [328]. The formation of acetaldehyde has been reported from the oxidation of ethylene by molecular oxygen. The solution contains $Pd(PPh_3)_4$ in a mixture of dioxane and CF_3CO_2H. Triphenylphosphine oxide is also formed, and added CO is converted to CO_2 [329]. The oxidation of ethylene by $PdCl_2$ in ethanol solvent is first-order in each reactant, and the mechanism is similar to the one in aqueous solutions [330]. The oxidation of 1,3-cyclohexadiene with $PdCl_2$ in acidic medium has been investigated [331].

Substituted stilbenes have been prepared by the coupling reaction between styrene and p-substituted anilines. The reaction is catalyzed

$$\underline{p}\text{-}XC_6H_4NH_2 + PhCH{=}CH_2 \longrightarrow \underline{p}\text{-}XC_6H_4CH{=}CHPh + NH_3$$

$$(X = H, Me, OMe, Cl, NO_2)$$

by palladium acetate in an acetic acid-dioxane solvent mixture [332]. Palladium chloride is used as an *in situ* source of palladium metal for the coupling of iodobenzene with phenylmagnesium bromide [333]. A mixture of $NiCl_2(PPh_3)_2$, PPh_3, and Zn in dry DMF has been used to promote the coupling reaction of aryl bromides to biaryls [334]. The palladium acetate-triphenylphosphine mixture has been used to promote the coupling of aryl halides and double bonds to give substituted indoles [335]. The reaction of phenyl compounds Ph_nA and Ph_nAX_2 ($n = 2,3$; A = P, As, Sb, Bi, S, Se, Te; X = Cl or $X_2 = O$) with Pd(II) salts in the presence of olefinic compounds (1-octene, ethyl acrylate) gives phenyl migration from A to Pd with subsequent phenylation of the olefin. The compound $Pd(OAc)_2$ is most effective. A mechanism involving nucleophilic assistance by acetate ion, when Pd(II) attacks the aromatic center electrophilically at the C atom bonded to A, is suggested [336]. Catalytic allylation of aryl halides with allyltributyltin occurs in the presence of $Pd(PPh_3)_4$ [337].

$$ArX + Pd(0) \longrightarrow \text{"ArPdX"}$$

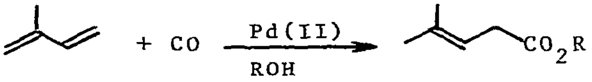
$$\text{"ArPdX"} + CH_2{=}CHCH_2SnBu_3 \longrightarrow ArCH_2CH{=}CH_2 + SnXBu_3 + Pd(0)$$

An optically active chiral bidentate phosphine ligand, 2,2'-bis(diphenylphosphinomethyl)-1,1'-binapthyl has been prepared. The nickel complex has been used for vinyl- and aryl-halide coupling reactions [338].

The acetoxylation of ethylene is catalyzed by salts of palladium(II) in the presence of organic nitrates [339]. The catalysis by platinum(II) complexes of the acetylation of pyridinic alcohols by N-acetylimidazole has been used for a range of alcohols [340]. Palladium(II) compounds have also been used as catalysts for the synthesis of dimethyl formamide from dimethyl amine, carbon dioxide, and hydrogen [341]. The carbonylation of isoprene in alcohol is

$$Me_2NH + CO_2 + H_2 \xrightarrow{PdCl_2} Me_2NCHO$$

catalyzed by palladium acetate and triphenylphosphine, and gives 4-methyl-3-pentenoate selectively. No dimerization-carbonylation



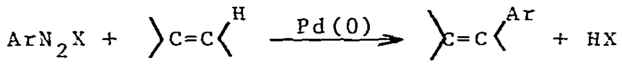
of isoprene occurs to give C_{11} esters [342]. Carbonylation of butadiene in t-BuOH is catalyzed by a mixture of $Pd(OAc)_2$ and PPh_3 to give t-butyl-3,8-nonadienoate [343]. The compound $Pd(PPh_3)_4$ can be used as a catalyst for the conversion of vinyl halides into vinyl cyanides with KCN. The yields are greater than 85% [344]. The

$$R^1R^2C{=}CR^3X + KCN \xrightarrow{Pd(PPh_3)_4} R^1R^2C{=}CR^3(CN) + KX$$

catalyst system $Ni(1,5\text{-}COD)_2/Ph_2P(CH_2)_nPPh_2$ (n = 1,2,3,4) has been used to convert 1-hexyne and CO_2 into 4,6-dibutyl-2-pyrone, together with 1-hexyne oligomers [345]. The complex $Pd(PPh_3)_4$ can be used to promote the alkylation, arylation, and vinylation of acyl chlorides by organotin compounds [346]. Zerovalent palladium compounds have

$$RCOCl + R'_4Sn \xrightarrow{Pd(PPh_3)_4} RCOR' + R'_3SnCl$$

also been used in the arylation of olefins by arenediazonium salts [347].

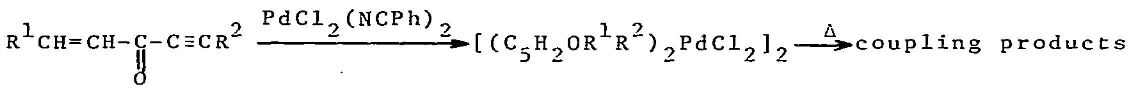


The oxidation of cyclohexene, cyclooctene, 3,3-dimethylbutene-1, hexene-1, and cis-hexene-2 by oxygen is catalyzed by palladium acetate. Trimeric palladium acetate is catalytically active but is converted by olefins into complexes of the type $[Pd_3(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_4]$. The products from the oxidation are the acetates [348]. The stereospecific formation of threo-1,2-dideuterio-2-chloroethanol in the Wacker reaction of trans-1,2-dideuterioethylene supports the idea that the hydroxypalladation step is a trans-process [349]. In the palladium-catalyzed hydrocarboxylation of α-methylstyrene using PPh_3 and (−)-DIOP as ligands, the optical yield depends on the proportions of phosphine and shows a maximum for a molar ratio of 2 [350]. The compound $Hg(C{\equiv}CPh)_2$ reacts with CO and alcohol in the presence of Pd(II) salts to form dialkyl phenylmaleate, along with small quantities of alkyl phenylpropiolate and dialkyl phenylfumarate [351].

Ligand stabilized Pd(II)-tin(II) chloride complexes such as $PdCl_2(P(\underline{p}\text{-tol})_3)_2\text{-}SnCl_2$ catalyze the regioselective carbonylation of 1-alkynes. Linear α,β-unsaturated acid esters are obtained in up to 96 mol% selectivity under mild conditions [352]. The effects

$$RC{\equiv}CH + CO + R'OH \longrightarrow RCH{=}CHCO_2R'$$

of ligand basicity and cone angle are considered. A mechanism involving the hydride $PdH(SnCl_3)(PPh_3)L$ is proposed. A mixture of nickel compounds and phosphine ligands can be used to catalyze the rearrangement of allyl but-3-enoate to heptadienoic acids [353]. Ethyl vinyl ketones form complexes (190) with $PdCl_2(NCPh)_2$. Upon heating, these complexes decompose to cyclic organic dimers [354].



$$R^1CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}C{\equiv}CR^2 \xrightarrow{PdCl_2(NCPh)_2} [(C_5H_2OR^1R^2)_2PdCl_2]_2 \xrightarrow{\Delta} \text{coupling products}$$

(190)

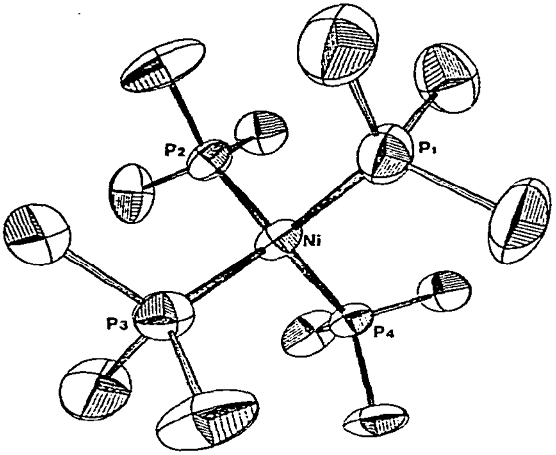
XIV. Complexes and reactions of general interest

A review has been published on the isocyanide complexes of Ni(0), Pd(0), and Pt(0), along with their complexes with O_2, the stereochemistry of metal-carbon bond formation, and the strong basicity of $PtL_n\text{-}H_2O$ [355]. Complexes $M(PPh_3)_4$ (M = Pd, Pt) have been prepared from compounds *cis*-$MCl_2(PPh_3)_2$ and alkaline alkoxides. The method is potentially useful as a means of *in situ* generation of low-valent species [356]. A review has been published covering hydrides and carbonyls of the platinum metal series [357]. The complex

$$\underline{cis}\text{-}PtCl_2(PPh_3)_2 + 2KO\text{-}\underline{t}\text{-}Bu \longrightarrow Pt(O\text{-}\underline{t}\text{-}Bu)_2(PPh_3)_2 \longrightarrow$$

$$Pt(OH)_2(PPh_3)_2 \xrightarrow[-OPPh_3]{PPh_3} Pt(PPh_3)_4$$

$[NiMe(PMe_3)_4]BPh_4$ undergoes dissociative reduction to the 17-electron molecule $[Ni(PMe_3)_4]BPh_4$ (191). The structure shows the cation and anion to be isolated from each other and the geometry about the nickel is tetrahedral. The magnetic moment is 2.40 B.M. [358]. The structure of $Pt(PCy_3)_3$ consists of $Pt(PCy_3)_3$ units packed together by



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(191)

three-fold screw axes. The average Pt-P distance of 2.303(13)Å is significantly longer than that of 2.231(6)Å found in $Pt(PCy_3)_2$. The platinum atom is only 0.04Å away from the P_3 plane. The temperature-dependent equilibria between $Pt(PCy_3)_3$, $Pt(PCy_3)_2$, and PCy_3, is discussed [359]. A range of organoplatinum chemistry is reported for the ligand P-_t_-Bu_2(C≡CPh). Protonation reactions to give hydrides, along with substitution reactions of alkyl and olefin complexes, are described [360].

The redox behavior of $M(PPh_3)_4$ (M = Ni, Pd, Pt) has been studied in DMF, DMSO, acetonitrile, propanediol carbonate, N,N-dimethylthioformamide, N-methylpyrrolidine-2-thione, and nitromethane [361]. The Pd and Pt complexes undergo two-electron irreversible oxidations with partial loss of ligand, and $Ni(PPh_3)_4$ is "reversibly" oxidized to a monovalent form followed by a reversible oxidation to a divalent form. The complex $Ni[HPPh_2]_4$ exchanges ligands with phosphites and gives pentacoordinate compounds $NiX_2[HPPh_2]_3$ with HgX_2 (X = Cl, Br, I, SCN). The oxidative addition of RX is believed to proceed by a radical pathway involving sequential oxidative addition and reductive elimination steps [362].

Carbonyl sulfide reacts with $Pt(PPh_3)_3$ under a range of conditions to give the complexes $Pt(COS)(PPh_3)_2$, $Pt_2S(CO)(PPh_3)_3$, and two new compounds of stoichiometry $Pt(COS)_2(PPh_3)_2$ [363]. The oxidative addition of $(SeCN)_2$ to $M(PPh_3)_4$ (M = Pd, Pt) gives complexes _trans_-$M(SeCN)_2(PPh_3)_2$ (192) with Pt-Se bonds. Dissolution in CH_2Cl_2 or DMF gives partial isomerization to the N-bonded form [364]. A series

$$M(PPh_3)_4 + (SeCN)_2 \longrightarrow \underline{trans}\text{-}M(SeCN)_2(PPh_3)_2 + 2\ PPh_3$$

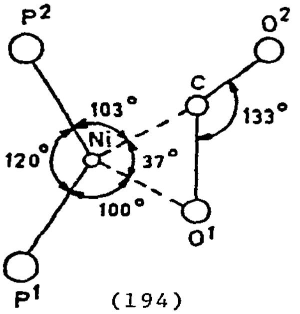
(192)

of thiolate platinum(II) complexes have been prepared by treating $PtCl_2(PPh_3)_2$ with a dithiol and base. The interesting compound $Pt(SH)_2(PPh_3)_2$ (193) has been reported, along with chelate complexes of 1,3-propanedithiolate, and the complex bis(triphenylphosphine)-1-platina-2,4,6-trithiacyclohexane [365]. A comprehensive article on the chemistry of complexes PdL_2 and PtL_2 has appeared where L is

$$\underline{cis}\text{-}PtCl_2(PPh_3)_2 + 2\ H_2S \xrightarrow{K_2CO_3} \underline{cis}\text{-}Pt(SH)_2(PPh_3)_2$$

(193)

a phosphine with a bulky substituent [366]. Ligand exchange chemistry is investigated, along with the reactions with O_2, olefins, HX and other small molecules. The reaction of NiL_4 (L = PEt_3, $P(n\text{-}Bu)_3$) with CO_2 gives a complex $Ni(CO_2)L_2$ (194) via the $Ni(CO_2)L_3$ species. The compound $Ni(CO_2)(PCy_3)_2$ reacts with O_2 to give the peroxocarbonato



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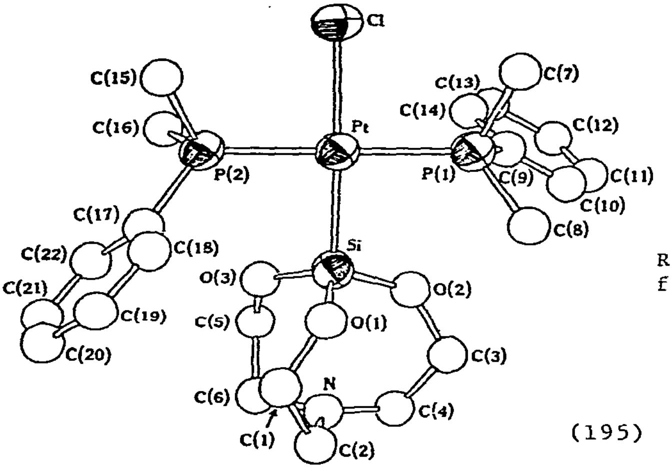
complex $Ni(CO_4)(PCy_3)_2$ [367]. The structure of $PtCl[Si(OCH_2CH_2)_3N](PPhMe_2)_2$ (195) shows a tetrahedral silicon coordinated to platinum,



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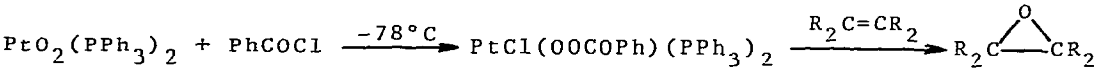
(195)

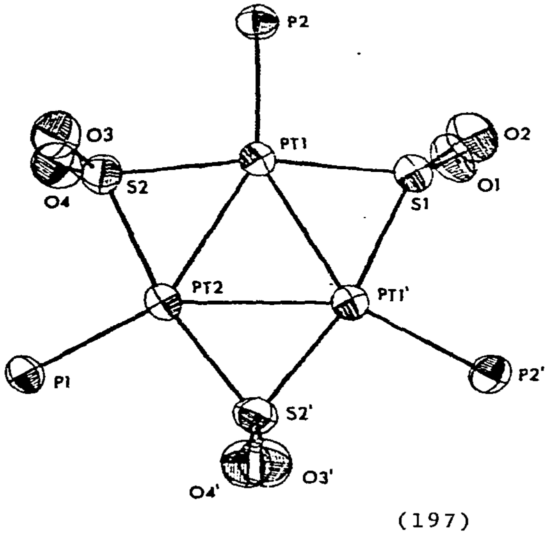
and a non-bonding Si-N distance of 2.89(1)Å [368]. Rigid, unsymmetrical cis-olefinic diphosphines $Ph_2PCH{=}C(R^1)PR^2R^3$ can be prepared by the stereospecific addition of secondary phosphines R^2R^3PH across the triple bond of a phosphorus coordinated phosphinoacetylene in cis-$MCl_2(Ph_2PC{\equiv}CR)_2$ (M = Pd, Pt) [369]. Treating the complex $PtO_2(PPh_3)_2$ with PhCOCl at -78°C gives a cis-chloroperoxybenzoatobis (triphenylphosphine)platinum(II) complex (196). The complex reacts rapidly with triphenylphosphine at -78°C to give triphenylphosphine oxide, and addition of norbornene or cyclohexene to the reaction mixture, followed by warming to room temperature, results in the



$$PtO_2(PPh_3)_2 + PhCOCl \xrightarrow{-78°C} PtCl(OOCOPh)(PPh_3)_2 \xrightarrow{R_2C=CR_2} R_2C\overset{O}{\text{—}}CR_2$$

(196)

formation of the epoxide [370]. Nickel nitrosyl cations $[Ni(NO)L_n]^+$ (L = PPh_3, n = 2,3; L = $PMePh_2$; n = 3) have been prepared from $Ni(CO)_2L_2$ and $NOPF_6$. The chemistry of the compounds with nucleophiles is reported and discussed [371]. Slow removal of SO_2 from a toluene solution of $Pt(SO_2)_2(PPh_3)_2$ yields the orange complex $Pt_3(SO_2)_3(PPh_3)_3$ (197) [372]. The structure consists of a triangle of Pt atoms, each of which is bonded to two bridging SO_2 groups and a PPh_3 molecule. An article has been published on ^1H NMR spectral work on N-bonded hydrazone complexes $PdCl_2(MePhN{-}N{=}N{=}C(Me)CHMe_2)_2$ [373]. The Si-Si metathesis reaction is catalyzed by $Pd(PPh_3)_4$ and other Ni and Pd complexes



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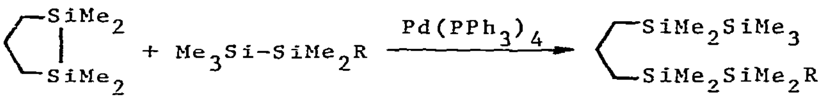
(197)

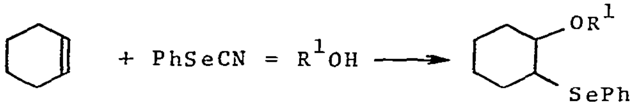
[374]. The addition reaction across $Pt(PPh_3)_3$ has been used to prepare complexes of type (198) having metal chains. The article reports the preparation of complexes with Pt and Hg, Cd, Zn and Ge [375].



$$Pt(PPh_3)_3 + [(C_6F_5)_3Ge]_2M \longrightarrow (C_6F_5)_3GeMPt(PPh_3)_2Ge(C_6F_5)_3 + PPh_3$$

(M = Hg, Cd, Zn) (198)

Copper or nickel halides have been used in the addition of alkyl or aryl selenocyanates to olefins to give β-oxy selenides (199) in high yields [376]. The coupling reaction between alkynylzinc chloride and an alkenyl iodide is catalyzed by phosphine-palladium compounds [377]. The compound $Ni(PPh_3)_4$ has been used in the arylation of olefins between haloaryls and vinylzirconium compounds [378].



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Extended Hückel calculations have been reported for icosahedral platinaboranes and carbaboranes $[B_{11}\{Pt(PH_3)_2\}H_{11}]^{2-}$, $[B_{10}C\{Pt(PH_3)_2\}H_{11}]^-$, and $B_9C_2[Pt(PH_3)_2]H_{11}$. The failure of the polyhedral skeletal electron-counting rules is attributed to the unequal bonding capabilities of the platinum $5d_{xz}$ and $5d_{yz}$ orbitals in the $Pt(PH_3)_2$ fragment. Analogous d^8 metal compounds are predicted to be stable [379].

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