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Review

Platinum–alkynyl and –alkyne complexes: old systems with new chemical and physical perspectives

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Abstract

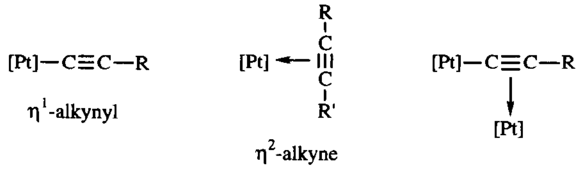
The chemistry of alkynyl and alkyne ligands in platinum complexes of different oxidation states is described. The review focuses on the synthetic aspects of mono- and polynuclear compounds and on the reactivity of σ-alkynyl and π-alkyne species in different stoichiometric reactions such as insertion, addition of nucleophiles and electrophiles, rearrangements and isomerization processes and also some catalytic additions of heteroatoms (B, Si, S) across the C≡C triple bond. The relevant features of polynuclear complexes bearing the C≡C group in dendrimers and organometallic polymers are briefly reported. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Alkynes; Alkynyls; Mono- and polynuclear complexes

1. Introduction

The chemistry of metal–alkynyl and –alkyne complexes, started more than 30 years ago [1], has undergone a significant development in recent years as a consequence of the ability of the C≡C group to display a versatile reactivity, peculiar nonlinear optical, liquid crystal and photophysical properties.

The C≡C triple bond of alkynes may interact with platinum metal centers giving rise to η^1-alkynyl and η^2-alkyne complexes [2], where the η^1-alkynyl systems can give subsequent η^2-coordination to form polynuclear derivatives [2].



The electronic features of the mononuclear η^1-alkynyl ligands bound to a single metal center have been extensively described from a theoretical point of view [3a] on the basis of vibrational spectroscopic and X-ray crystallographic data. In most of the complexes studied, the alkynyl ligand is found to be a good σ- and π-donor, but a poor π-acceptor. Photoelectron spectroscopic studies together with Hartree–Fock–Slater molecular orbital calculations on the series of *trans*-$[M(C{\equiv}CR)_2(PH_3)_2]$ (M = Pd, Pt; R = H, Me) complexes [3b] showed that the M–C≡CR π-backbonding is unimportant. The electron population of π*(C≡CR) is no greater than 0.05 e^- and net destabilizating interactions between the occupied π-symmetry metal and π(C≡CR) orbitals are strong. The electronic spectra of the *trans*-$[M(C{\equiv}CR)_2L_2]$ (M = Pd, Pt; L = phosphine, stibine) complexes have been extensively studied [3c]. They show three intense (ε ca. 10^4) bands in the 200–350 nm region and can be explained assuming that the lowest-energy band arises from a transition between the π(C≡CR) and the π*(C≡CR) orbitals, and the CT transitions from π(C≡CR) to the metal $(n+1)$p orbitals. The X-ray data show that the C≡C bond lengths (aver-

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age value 1.20 Å) in most compounds are slightly elongated relative to those of organic terminal alkynes (average value 1.17 Å) as a result of extremely low or no M → C≡CR π-backbonding, as supported also by the Pt–C bond lengths that differ from those of the corresponding alkyl complexes by only ca. 0.08 Å.

The *trans* influence of the alkynyl ligand has been studied in a series of compounds of the type *trans*-$[Pt(X)Cl(PPh_{3-n}R_n)]$ ($n = 0$ or 1) from X-ray and NMR determinations [3a] that have led to the following order of the *trans* influence of the X ligands:

X: $C(O)R \geq C(sp^3) \geq C(sp^2) > H \gg C{\equiv}CR \gg Cl$

As for η^2-alkyne derivatives, the Pt(II) complexes are relatively rare and theoretical calculations showed that the perpendicular coordination is preferred in tetracoordinate planar Pt(II) complexes [4]. Ab initio calculations have been reported also for five-coordinate platinum(II)–alkyne complexes of the type $[PtX_2(Me_2\text{-}phen)(alkyne)]$ (X = halogen; Me_2phen = 2,9-dimethyl-1,10-phenanthroline), showing that in analogous systems ethylene exhibits better σ-donating and π-accepting properties than acetylene [5]. In particular, the coordinated diphenylacetylene shows a C≡C bond length and a bending back of the phenyl groups with respect to the C≡C triple bond axis, which are intermediate between those found for the trigonal Pt(0) and the square planar Pt(II) species [5].

Also a number of Pt(0)–π-alkyne complexes of the type $[PtL_2(\eta^2\text{-alkyne})]$ (L = tertiary phosphine) and $[Pt(\eta^2\text{-alkyne})_2]$ have been reported [6a]. On coordination to Pt(0), the C≡C bond is lengthened and substituents on the triple bond are bent away from the metal center, either in the presence of electron-withdrawing or electron-donating groups. Recently, the chemistry of Pt(0) and Ni(0) π-cycloalkyne and -aryne complexes has been extensively reviewed [6b].

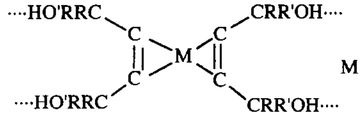
Here we shall describe recent results on the synthesis of mononuclear, homo- and hetero-polynuclear platinum–alkynyl and –alkyne complexes and their reactivity in some stoichiometric and catalytic processes. The description of the different aspects of the chemisorption processes of alkynes on platinum surfaces, involving C–C and C–H activation, ubiquitous in the catalytic cracking and reforming processes used in petrochemical industry, is out of the scope of the present review [7].

2. Mononuclear Pt(0)–alkyne complexes

Complexes of the type $[M(0)(\eta^2\text{-alkyne})_2]$ (M = Pt, Pd) are of relevant interest not only as starting materials for organometallic reactions, but also as model compounds for understanding the interaction of an alkyne with metal surfaces [7].

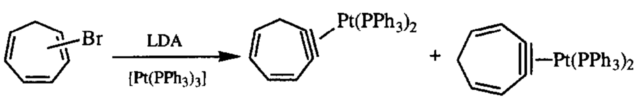
The preparation of the first bis(acetylene)Pt(0) complex has been reported [8] to proceed by reacting $[Pt(COD)_2]$ with an excess of diphenylacetylene leading to pale yellow crystals of $[Pt(PhC{\equiv}CPh)_2]$, which then have been reacted with PMe_3 to give $[Pt_2(PMe_3)_2(PhC{\equiv}CPh)_2]$. The structures of both complexes were determined by X-ray diffraction analysis.

Similarly, by reacting $[Pt(COD)_2]$ or [Ni(cdt)] (cdt = 1,5,9-cyclododecatriene) with the alkynols $Me_3CC{\equiv}CCMe_2OH$ and $Me_2C(OH)C{\equiv}CCMe_2(OH)$, the corresponding $(alkyne)_2M$ complexes have been obtained [9]. Single-crystal X-ray structure determinations reveal that the central metal atom is tetrahedrally coordinated by the four carbon atoms of the alkyne ligands and that two $(alkyne)_2M$ units are connected via hydrogen bonds between the four OH groups to form dimers or trimers in the solid state.



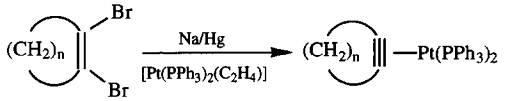
M = Ni, Pt; R, R' = Me, CH_2CHMe_2

The synthesis of tropynes and cyclic alkynes has been reported to occur by base-induced dehydrobromination from the corresponding bromoalkenes in the presence of $[Pt(PPh_3)_3]$ according to Eq. (1) [10a]:



LDA = lithium diisopropylamide (1)

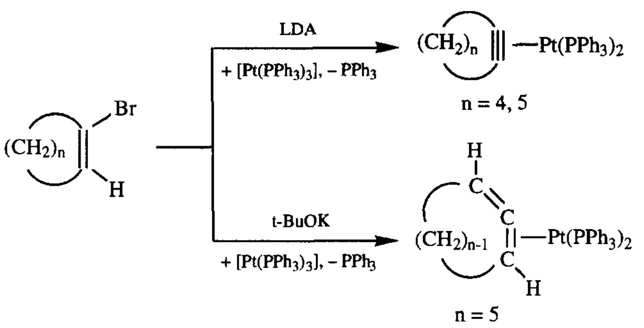
The reduction of the appropriate 1,2-dibromocycloalkene with 1% sodium amalgam in the presence of zerovalent metal complexes is reported to be a general method for the preparation of cyclic alkyne complexes of Ni(0), Pd(0) and Pt(0) [6b,c,10b] (Eq. (2)):



n = 4, 5 (2)

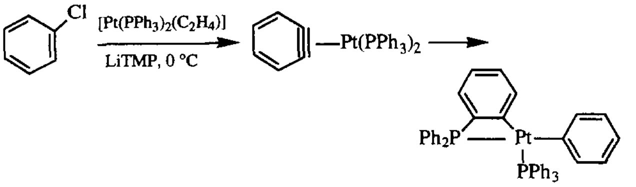
An alternative high-yield route to the $Pt(PPh_3)_2$ complexes of cyclohexyne and cycloheptyne is the treatment of the appropriate 1-bromocycloalkene and $[Pt(PPh_3)_3]$ with lithium diisopropylamide (LDA) [10c]. The use of *t*-BuOK instead of LDA gives dibenzannulated tropyne complexes, but affords the isomeric cyclic allene complex in the case of seven-membered rings (Scheme 1). The LDA reaction probably proceeds by base-promoted elimination of HBr from the transient intermediate $Pt(PPh_3)_2$ complex of the 1-bromocycloalkene, which could be detected in the absence of LDA, before giving isomerization processes.

Also the $[(\eta^2\text{-benzyne})Pt(PPh_3)_2]$ compound was generated by reduction of the appropriate (*o*-halogenoaryl)Pt(II) precursor with 43% sodium amalgam or by



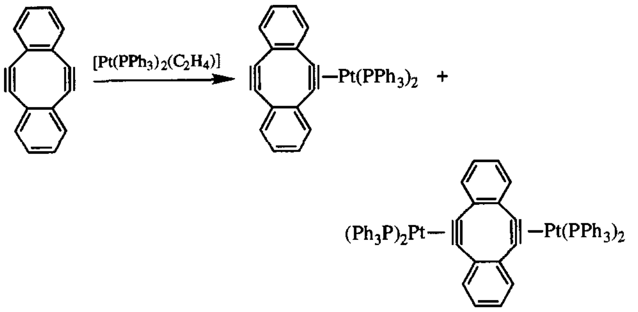
Scheme 1.

reaction of chlorobenzene with the non-nucleophilic base LiTMP (2,2,6,6-tetramethylpiperid-1-yl lithium) and $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)$ at 0°C. It was identified on the basis of spectroscopic data being less stable than the cyclohexyl and cycloheptyl analogues, giving isomerization in a few hours at room temperature according to Eq. (3) [11]:



(3)

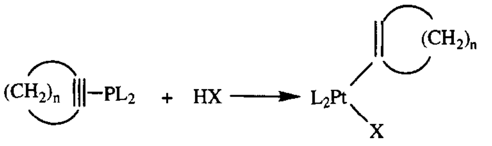
By ethylene substitution on $[Pt(PPh_3)_2(C_2H_4)]$ a series of unusually stable phenylene derivatives was obtained according to Eq. (4) [12]:



(4)

The synthesis of perhalogenated–alkyne complexes of the type $[Pt(PPh_3)_2(ClC{\equiv}CCl)]$ was reported to occur by reaction of dichloroethyne with $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$ [13a]. Subsequent reactions with phosphites have been described [13b] to give phosphine substitution or oxidative addition to form *cis*- and *trans*-$[Pt(PPh_3)_n\{P(OPh)_3\}_{2-n}Cl(C{\equiv}CCl)]$ ($n = 0,1$) depending on the reaction conditions.

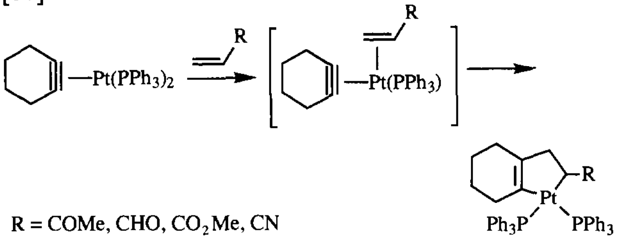
The reactivity of Pt(0)–cycloalkyne complexes with electrophiles proceeds with the cleavage of the metal–alkyne bond (Eq. (5)) [14] to give the corresponding η^1-alkenyl platinum(II) complexes:



n = 4, 5; X = Cl, OH, SPh, CH_2CN, OR; L_2 = phosphine or diphosphine

(5)

The insertion of electrophilic or strained olefins into the metal–cycloalkyne bond has been reported to give platinacyclopentenes (Eq. (6)). The observed regioselectivity suggests that this reaction proceeds by initial coordination of the olefin at the Pt center with PPh_3 displacement and subsequent attack of the alkyne on the electron-deficient carbon atom of the coordinated alkene [6b]:

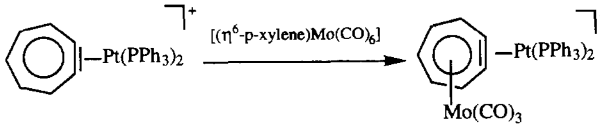


R = COMe, CHO, CO_2Me, CN

(6)

On the other hand, the corresponding insertion reactions of CS_2 and CO_2 on cyclohexyne complexes $[PtL_2(\eta^2\text{-}C_6H_8)]$ proceed only with more strongly basic bidentate ditertiary phosphines of the type $R_2PCH_2CH_2PR_2$ (R = Me, Et, Cy) [6b].

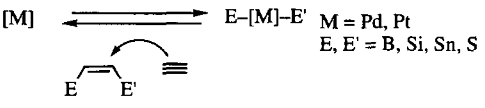
Platinum–molybdenum bimetallic complexes of cyclic tropynes and alkynes have been obtained [15] according to Eq. (7):



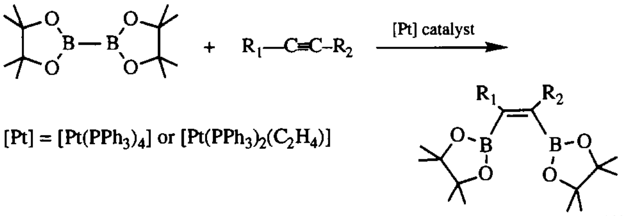
(7)

The Pt–Mo complex of reaction (7) has also been characterized by X-ray analysis and reduction processes by selective hydride addition have been described.

Relevant catalytic processes are suggested to proceed through Pt(0)–alkyne key intermediates [16] consisting in oxidative addition of inter-heteroatom bonds comprising S, B, Si, Sn. These reactions readily take place and trigger a variety of catalytic additions of the bonds to C–C unsaturated systems through the steps of an oxidative addition of an inter-heteroatom bond E–E′ to a transition-metal complex, the insertion of an alkyne into the Pt–E or Pt–E′ bond and finally reductive elimination of the products according to the general scheme



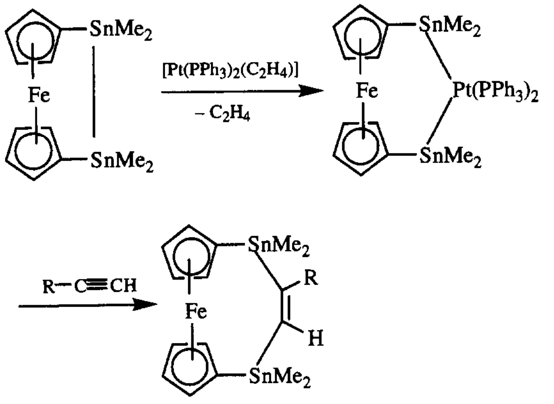
Within these catalytic systems, the most studied reactions are the diboration of alkynes [17] involving an alkyne insertion into the Pt–B bond to provide stereospecific *cis* bis-boryl alkenes in good yields, in particular using diboron reagents according to Eq. (8):



(8)

A theoretical study of the mechanism of the diboration reaction of alkynes has been carried out, indicating that the dissociation of a ligand on the Pt catalyst, which allows the coordination of the alkyne to form a π-complex, is the rate-determining step. The observed stereoselectivity has been explained in terms of the rigidity of the C–C π-bond [17d].

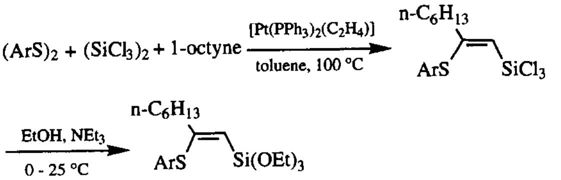
Pt(0) complexes also promote the distannation reaction of terminal alkynes bearing non-bulky substituents, which has been shown to proceed under mild conditions (Eq. (9)) [18]:



(9)

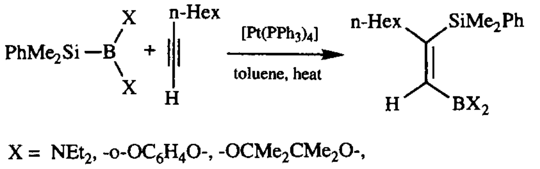
The use of another potential catalyst such as $[Pt(PPh_3)_4]$ was not successful due to the presence of free PPh_3.

As a new strategy to introduce two different heteroatoms into carbon–carbon unsaturated bonds, the first Pt(0)-catalyzed regio- and stereoselective thiosilylation of alkynes using disulfides and disilanes has been reported according to Eq. (10) [17e]:



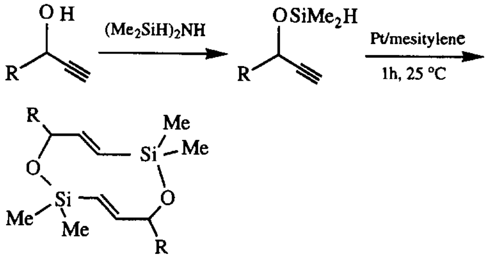
(10)

Silaboration of a variety of terminal alkynes [19] takes place with good regio- and stereoselectivity to afford Z-1-boryl-2-silylalkenes in high yield catalyzed by $[Pt(PPh_3)_4]$ according to reaction (11):



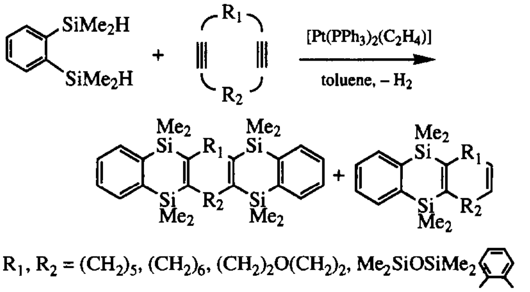
(11)

Unusual Pt-catalyzed stereo- and regioselective intramolecular hydrosilylation of propargyl alcohols to give E,E-5,10-dialkyl-2,2,7,7-tetramethyl-1,6-dioxa-2,7-disila-3,8-ecidienes was also described (Eq. (12)) [20]:



(12)

$[Pt(PPh_3)_2(C_2H_4)]$ catalyzes the dehydrogenative double silylation reaction of 1,2,4,5-tetrakis(dimethylsilyl)benzene with cyclic dyines to give ladder polycarbosilanes (Eq. (13)) [21].



(13)

It is noteworthy that the reaction of terminal alkynes and 1-hexyne with $[Pt(PPh_3)_2(C_2H_4)]$ in the presence of disilacyclobutene compounds affords a mixture of products of the type **A**–**C** (Scheme 2) [22] without formation of the corresponding benzenes obtained in the presence of Pd(0) systems.

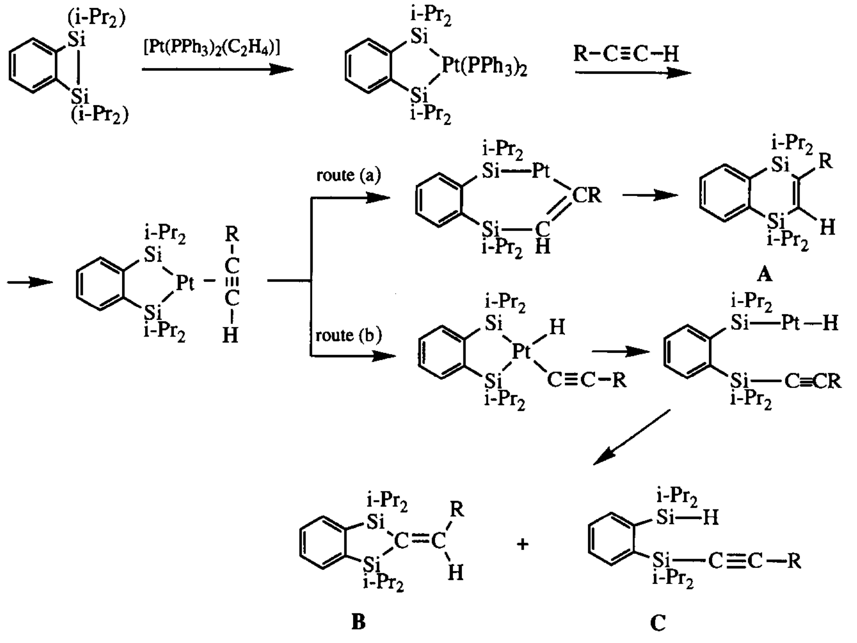
The proposed mechanism involves the formation of a π complex, and insertion of the triple bond into the Pt–Si bond (route (a)) or C–H bond activation leading to hydride complex (route (b)) followed by 1,2 shift of an alkynyl group to one of two silicon atoms to give **B** and **C**.

The mechanism of Pt(0)-mediated hydrogenation of alkynes [23] has been studied through parahydrogen-induced polarization showing pairwise transfer of hydrogen to the unsaturated substrates.

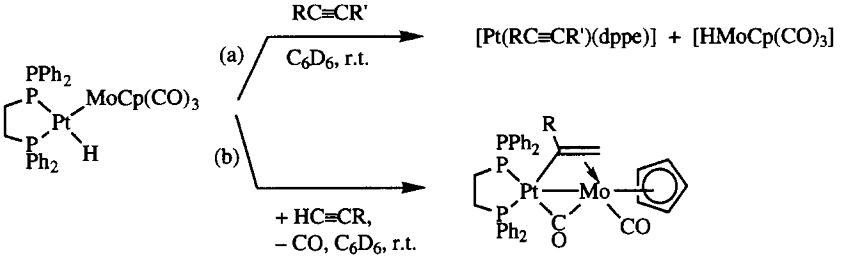
Finally, a Pt(0)(η^2-alkyne) complex is reported to be formed from the reaction of $[(dppe)HPt–MoCp(CO)_3]$ [24] with disubstutued alkynes according to Scheme 3 (route (a)). However, in the presence of terminal alkynes the Markovnikov addition of $[HMoCp(CO)_3]$ to the coordinated alkyne takes place to give the new heterodinuclear alkenyl complexes $[(dppe)(\mu\text{-}H_2C{=}CR)Pt–MoCp(\mu\text{-}CO)(CO)]$ (route (b)).

3. Pt(I)–alkyne complexes

A dinuclear Pt(I)–dimethylacetylene dicarboxylate complex $[Pt_2(CO)_2(PPh_3)_2(C_2R_2)]$ was prepared by reac-

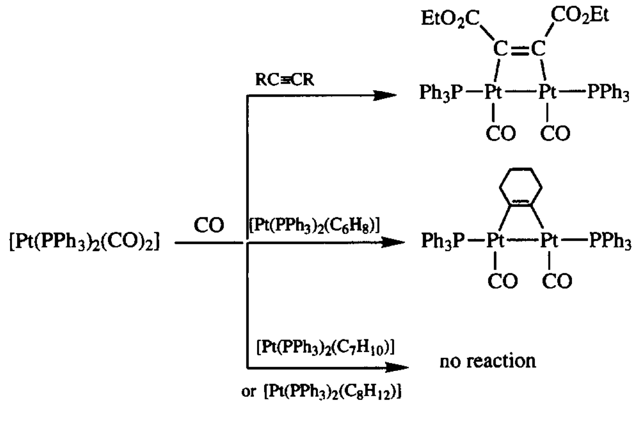


Scheme 2.



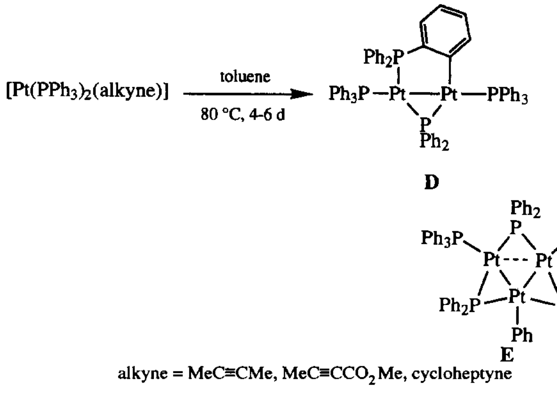
Scheme 3.

tion of $[Pt(PPh_3)_2(CO)_2]$ with R_2C_2 ($R = CO_2CH_3$) under an atmosphere of carbon monoxide [25], where the alkyne behaves as a ligand bridging the Pt–Pt moiety of the dinuclear Pt(I) complex. In this reaction, mediated by CO, the alkyne ligand serves as the oxidizing agent. It is noteworthy that the platinum(0)–cyclohexyne complex reacts with CO to form $[Pt_2(PPh_3)_2(CO)_2(C_6H_8)]$, while cyclic alkyne complexes with less strained alkynes such as cycloheptyne or cyclooctyne were inert to CO addition due to lower electrophilic character of the alkyne ligands (Scheme 4).



Scheme 4.

New dinuclear Pt(I) complexes of type **D** can be obtained, in about 60% yield, together with trinuclear compounds of type **E**, from thermal degradation of various complexes of the type $[Pt(PPh_3)_2(alkyne)]$ in toluene (Eq. (14)) as a result of both C–H and P–Ph cleavage of coordinate PPh_3 [26].



(14)

In the case of the dimethylacetylenedicarboxylate complex $[Pt(PPh_3)_2(MeO_2CC{\equiv}CCO_2Me)]$, on heating in toluene, the cyclometallation product $[\overline{Pt\{C_6H_4(P}Ph_2)\}\{\eta 1\text{-}C(CO_2Me){=}CHCO_2Me\}(PPh_3)$ is quantitatively obtained.

4. Mononuclear Pt(II) complexes

4.1. Synthetic procedures

Alkynes interact with Pt(II) substrates giving rise to different products depending on the reaction conditions [2]. By displacement of a halide in water with soluble acetylenes (Eq. (15)) η^2-complexes are directly obtained:

$$K_2PtCl_4 + Me_2(OH)CC{\equiv}CC(OH)Me_2 \xrightarrow{H_2O} K[PtCl_3\{Me_2(OH)CC{\equiv}CC(OH)Me_2\}] + KCl \quad (15)$$

or by addition of a silver(I) salt [27] (Eq. (16)):

$$trans\text{-}[Pt(Cl)(CH_3)L_2] + RC{\equiv}CR' \xrightarrow{AgPF_6} trans\text{-}[Pt(CH_3)L_2(RC{\equiv}CR')]PF_6 + AgCl \quad (16)$$

$R,R' = $ alkyl, aryl; $L = $ phosphine, arsine

The deprotonation reaction of the slightly acidic proton of terminal alkynes with a base (such as n-BuLi, Ag_2O, NaOH, KOH, NH_3, $NHEt_2$) yields the acetylide $RC{\equiv}C(-)$, which then affords the η^1-alkynyl complexes by reaction with neutral and cationic complexes containing labile ligands. For instance, *trans*-$[Pt(C_6F_5)_2(tht)_2]$ (tht = tetrahydrothiophene) reacts with $LiC{\equiv}CR$ (R = $SiMe_3$, Ph, t-Bu) in diethyl ether or THF leading to the novel dianionic species *trans*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ [28] (Eq. (17)):

$$trans\text{-}[Pt(C_6F_5)_2(tht)_2] + 2LiC{\equiv}CR \xrightarrow{Et_2O \text{ or } THF} trans\text{-}[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-} \quad (17)$$

R = Ph, $SiMe_3$, t-Bu

Again σ-acetylide complexes can be obtained according to reaction (18) [29]:

$$trans\text{-}[Pt(R')(Cl)L_2] \xrightarrow[-AgCl]{+Ag^+,\ solv} trans\text{-}[Pt(R')L_2(solv)]^+ \xrightarrow{-C{\equiv}CR} trans\text{-}[Pt(R')(C{\equiv}CR)L_2] \quad (18)$$

R = aryl; $R' = CH_3$, CF_3; L = phosphine, arsine

The most common method to prepare platinum ethynyls of the type $[Pt(C{\equiv}CR)_2L_2]$ (L = phosphine) (see for instance Eq. (19)) uses CuI as a catalyst [30]. The reaction likely proceeds through the formation of copper ethynyls as intermediates. Unless L_2 is a chelating diphosphine, the bis-ethynyls formed are mostly of *trans* configuration, even when starting from starting materials of *cis* geometry, the *trans* form being thermodynamically favoured (Eq. (19)).

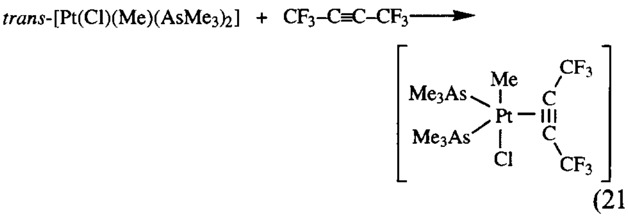
$$cis\text{-}[PtCl_2(PMePh_2)_2] + 2PhC{\equiv}CH \xrightarrow[CuI]{NHEt_2} trans\text{-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] \quad (19)$$

Stable *cis*-$[Pt(C{\equiv}CPh)_2L_2]$ have been obtained from the reaction of $PhC{\equiv}CH$ in the presence of NaOEt with $[PtCl_2(COD)]$, which readily decomposes [30c] (Eq. (20)):

$$[PtCl_2(COD)] + 2PhC{\equiv}CH \xrightarrow[EtOH]{NaOEt} [Pt(C{\equiv}CPh)_2(COD)] \xrightarrow{+2L} cis\text{-}[Pt(C{\equiv}CPh)_2L_2] \quad (20)$$

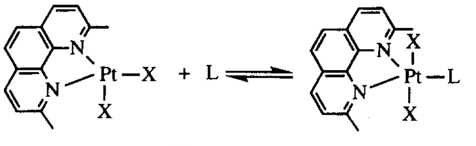
$L = PPh_3$, $PMePh_2$

In the absence of a silver(I) salt, the reaction of *trans*-$[PtCl(CH_3)(AsMe_3)_2]$ with $F_3CC{\equiv}CCF_3$ gave the corresponding five-coordinate complex containing the alkyne coordinated in a η^2 fashion, according to reaction (21) [31]:



(21)

The preparation of a series of five-coordinate Pt(II)-η^2-alkyne complexes of the type $[PtX_2(Me_2phen)(alkyne)]$ has been reported to proceed according to reaction (22), the stability of the final products depending on the halide (I > Br > Cl) and the presence of electron-withdrawing substituents on the alkyne. Such a reaction also led to a successful synthesis of the corresponding alkene complexes [5]:

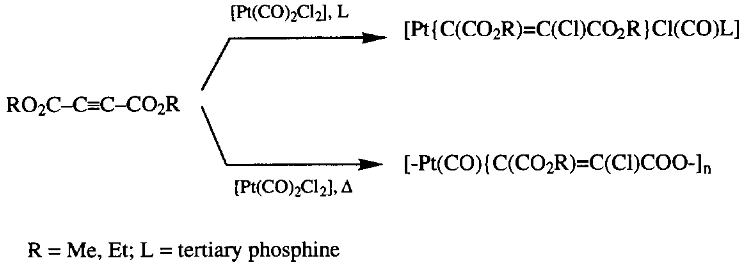


L = alkyne; X = halide

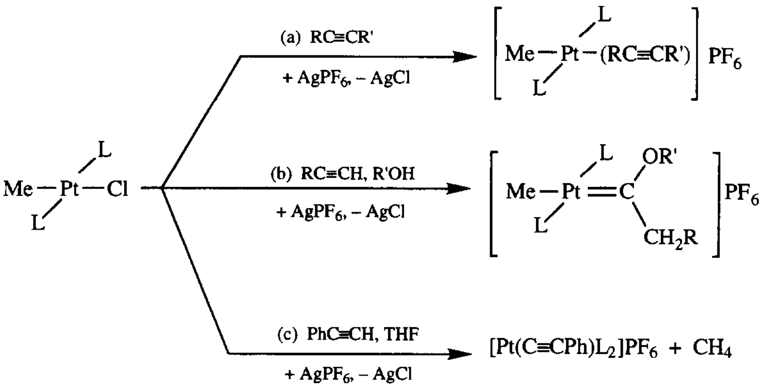
(22)

Alkyne complexes of Zeise's salt type $[K(18\text{-}cr\text{-}6)][PtCl_3(RC{\equiv}CR')]$ (R,R′ = Me, Et, n-Pr, Ph) have been prepared by reacting K_2PtCl_4 with crown ether 18-cr-6 in H_2O with internal alkynes. The alkyne ligand may then be displaced upon reaction with 1-pentyne affording the complex $[K(18\text{-}cr\text{-}6)][PtCl_3(n\text{-}PrC{\equiv}CH)]$, being the first example of such a type of complex with a terminal alkyne [32].

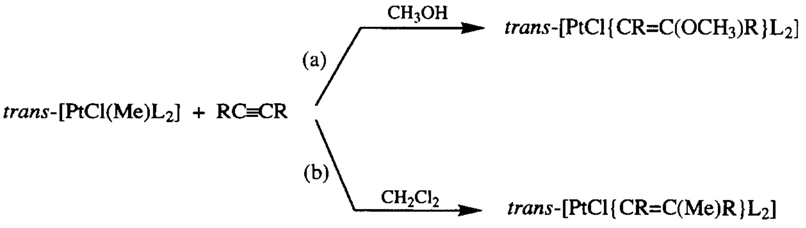
Alternative routes to η^2-alkyne complexes involve displacement of olefins as in the reaction of the Zeise's salt with acetylenes giving ethylene displacement with the formation of acetylene complexes of the type $K[Pt(RC{\equiv}CR)Cl_3]$ [2]. Furthermore, alkynes may undergo bridge cleavage as in the reaction with polymeric $[Pt(HBpz_3)(Me)]_n$ to afford monomeric five-coordinate complexes [33] (Eq. (23)):



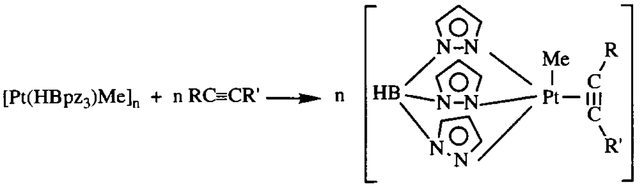
Scheme 5.



Scheme 6.



Scheme 7.



(23)

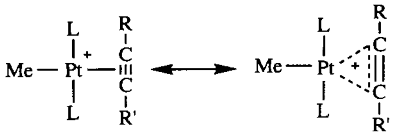
4.2. Miscellaneous reactions

It is noteworthy that different kinds of products such as olefins, alkynyls or carbenes can be obtained by reaction of alkynes with Pt(II) substrates depending on the alkyne, the substrate and the reaction conditions. For instance, monosubstituted alkynes can give polymerization in the presence of Pt(II) halides [2] or in a number of cases they insert into the Pt–Cl bonds [34] (Scheme 5).

The reaction of cationic platinum complexes of the type *trans*-$[Pt(CH_3)L_2(solv)]^+PF_6^-$ with acetylenes was reported [35] to depend markedly on the nature of substituents R and R′ of the acetylene, the nature of the ancillary ligands L, the solvent and the reaction conditions. Thus, the reaction of dialkyl- and diarylacetylenes in MeOH or acetone gave *trans*-$[PtCH_3(RC{\equiv}CR')L_2]PF_6$ (Scheme 6, route (a)), while monoalkylacetylenes and phenylacetylene in MeOH or EtOH gave cationic alkoxycarbene complexes (Scheme 6, route (b)). Reactions of monoalkyl acetylenes in aprotic polar solvents (i.e.THF) gave acetylide formation (Scheme 6, route (c)) accompanied by CH_4 elimination.

Similar reactions with disubstituted acetylenes RC≡CR′ containing electron-withdrawing groups R and R′ produce σ-vinyl ether complexes in MeOH, while in aprotic solvents insertion into the Pt–Me bond occurs (Scheme 7) [35].

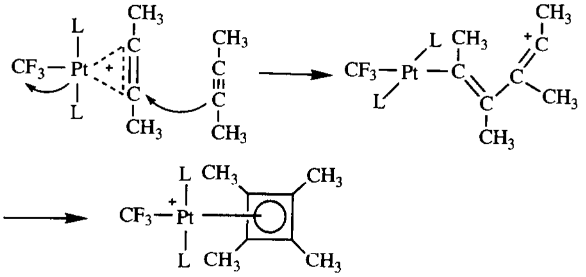
All these reactions were explained with the initial formation of ‘carbonium ions’ of the following type [35,36]:



which are then susceptible to intramolecular rearrangements and/or nucleophilic addition, according to reaction Scheme 8 [36].

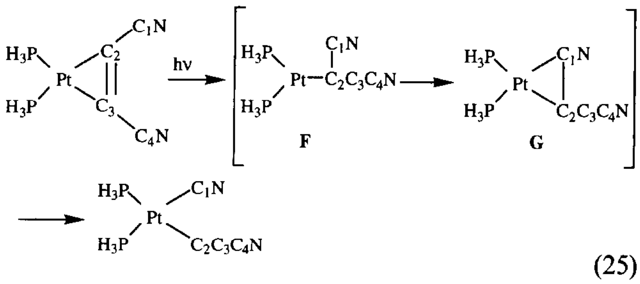
Carbene formation occurs with terminal alkynes in protic solvents such as MeOH, while in polar, but aprotic solvents, proton abstraction by the solvent takes place to give the acetylide. This type of process prevents the isolation of cationic terminal acetylene complexes, which on the other hand could be obtained with dialkyl or diarylacetylenes, which have been shown to react slowly with a nucleophilic protic solvent such as MeOH to give methyl vinyl ether complexes.

It is observed that either increasing the electrophilic character of the acetylene in the absence of a nucleophilic protic solvent or enhancing the electrophilic character of the organoplatinum cation upon introducing a CF_3 group in the coordination sphere makes, polymerization processes become accessible. In some instances reaction intermediates such a the tetramethylcyclobutadiene complex $[PtCF_3\{C_4(CH_3)_4L_2]PF_6$, can be isolated [36] (Eq. (24)):



(24)

The electronic mechanism of the thermal and photochemical isomerization of the dicyanoethylene complex $[Pt(PH_3)_2(NCC{\equiv}CCN)]$ to the acetylide derivative $[Pt(PH_3)_2(CN)(C{\equiv}CCN)]$ has been investigated theoretically [37]. In the thermal process, the decomposition reaction of $[Pt(PH_3)_2(NCC{\equiv}CCN)]$ into $\{Pt(PH_3)_2\}$ and $\{NCC{\equiv}CCN\}$ is favored, but the association of the separated fragments leads to the acetylene complex rather than the acetylide. On the other hand, the reaction can be photochemically induced, through the formation of three-coordinated Pt intermediates during the isomerization from the state **F** to **G** (Eq. (25)):



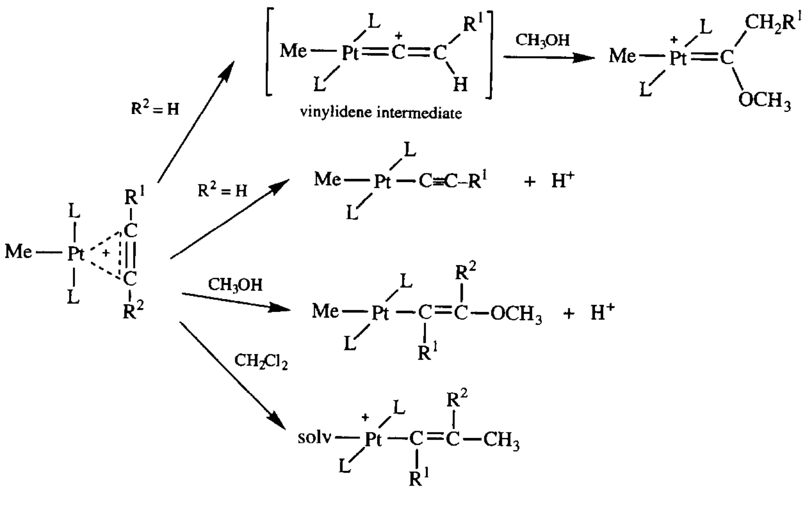
(25)

Insertion reactions are reported to occur in the Pt–H bond to form σ-enyl complexes as in the case of thioalkynes [38], where the formation of *cis* or *trans* products depends on the nature of the ancillary ligands on the Pt center and of the R and R′ substituents on the alkyne. The 1-thialkyl-1-enyl moieties are formed as *E* isomers (Scheme 9).

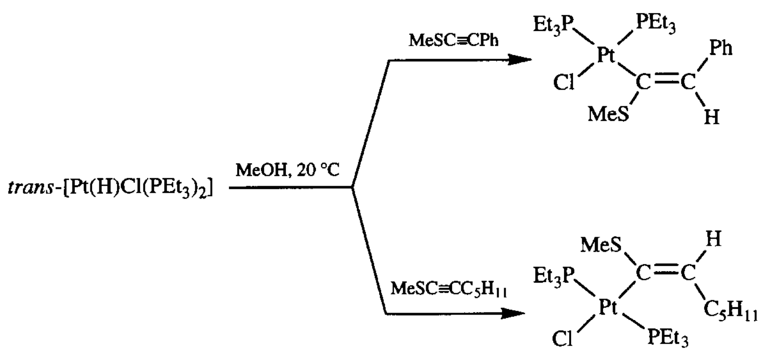
$PhSC{\equiv}CSiMe_3$ reacts with *trans*-$[PtClH(PPh_3)_2]$ with splitting of the trimethylsilyl group to generate *trans*-$[Pt\{E\text{-}C(SPh){=}CH_2\}Cl(PPh_3)_2]$ [38].

Dimethylacetylenedicarboxylate rapidly inserted into the Pt–NMe bond of the Pt(II) urylene complex $[Pt\{NMeC(O)NPh\}(COD)]$ to give $[Pt\{C(CO_2Me){=}C(CO_2Me)NMeC(O)NPh\}(COD)]$ (Scheme 10, route (a)) [39]. The diacetylide complex $[Pt\{C{\equiv}C(O)OMe\}_2(PPh_3)_2]$ has been obtained by reacting the more robust platinum urylene $Pt\{NMeC(O)NPh\}(PPh_3)_2]$ with methyl propiolate giving displacement of the urea dianion (Scheme 10, route (b)).

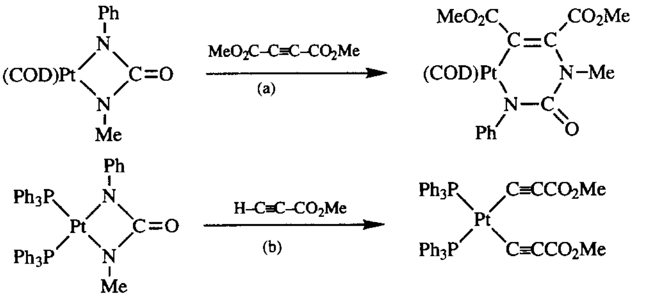
The cationic Pt–H complex *trans*-$[PtH(PPh_3)_2(THF)]^+$ reacts at low temperature with



Scheme 8.

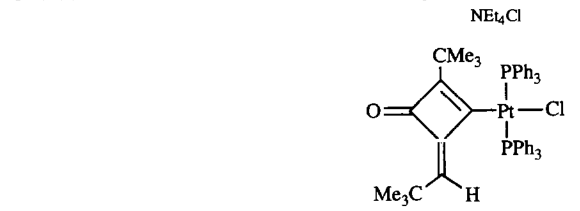


Scheme 9.



Scheme 10.

$O{=}C(C{\equiv}CCMe_3)_2$ to form the η^1-exoalkylidene cyclobutenone ligand (Eq. (26)) [40] through addition of the Pt–H bond to one of the alkynyl substituents of the dialkynyl ketone followed by an overall Pt-mediated insertion of the second alkynyl substituent into the resulting Pt–C(alkenyl) bond.



$$trans\text{-}[Pt(H)(PPh_3)_2(THF)]^+[SbF_6]^- + O{=}C(C{\equiv}CCMe_3) \xrightarrow[NEt_4Cl]{-78\text{ to }25\ °C}$$

(26)

Phenylacetylene reacts readily with *cis*-[Pt-Me(SiPh$_3$)L$_2$] [41] ($L = PMePh_2$, PMe_2Ph) giving the acetylene insertion products *cis*-[PtMe{C(Ph)=CH(SiPh$_3$)}L$_2$]. In contrast, *trans*-[PtMe(SiPh$_3$)L$_2$] complexes were totally inactive towards phenylacetylene insertion [41]. Phenylacetylene also reacts with the bis(silyl)platinum complexes [42] *cis*-[Pt(SiR$_3$)$_2$(PMe$_2$Ph)$_2$] ($SiR_3 = SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, $SiFPh_2$) to afford the insertion complexes *cis*-[Pt{C(Ph)=CH(SiR$_3$)}-(SiR$_3$)(PMe$_2$Ph)$_2$]. In the case of the reaction of acetylene, the complex *cis*-[Pt(CH=CHSiPh$_3$)-(SiPh$_3$)(PMe$_2$Ph)$_2$] was obtained and the structure was determined by X-ray diffraction study. Kinetic studies indicate that the insertion processes involved dissociation of a PMe$_2$Ph ligand followed by insertion of phenylacetylene into the Pt–SiR$_3$ bond.

4.3. Reactivity

Acetylenes coordinated to relatively electron-deficient Pt(II) substrates are activated towards insertion, rearrangements and nucleophilic attack processes. In contrast, coordination to a relatively electron-rich metal, as in the five-coordinate π-complexes, activates acetylenes to a much smaller extent and may indeed deactivate them towards such reactions [2].

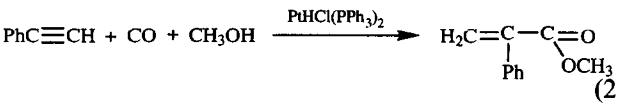
4.3.1. Insertion reactions

4.3.1.1. Pt–C bonds. Disubstituted alkynes having electron-withdrawing groups are known to give insertion reactions into the Pt–CH$_3$ bond of complexes of the type *trans*-[Pt(Me)XL$_2$] (L = tertiary phosphine, arsine, stibine) and *cis*-[PtMe(R$_2$Bpz$_2$)(acetylene)] to afford the corresponding platinum–(methyl)vinylic derivatives [43,44].

On the other hand, some Pt(II) complexes catalyze the linear polymerization of acetylenes: the process involves the initial formation of a σ-acetylide complex followed by successive acetylene insertion into the Pt–C σ-bond [45].

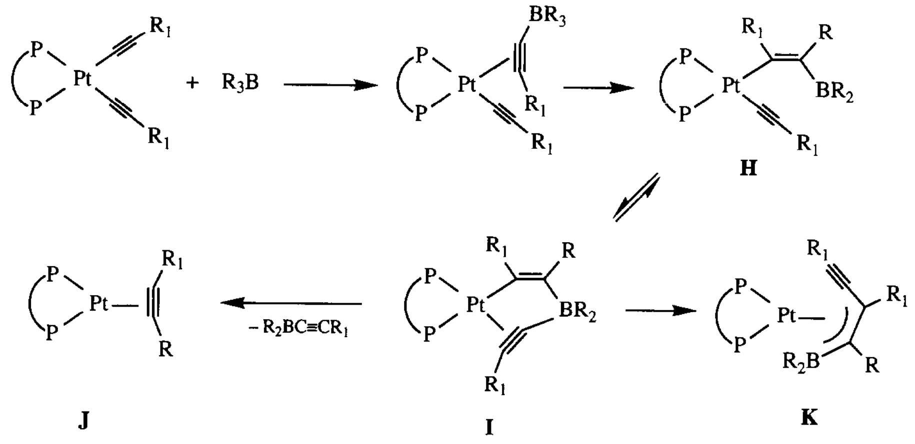
4.3.1.2. Pt–H bonds, the hydrogenation and hydromethoxycarbonylation of alkynes. Acetylenes can be hydrogenated in the presence of Pt(II)/Sn(II) systems [46a]. The mechanism of hydrogenation of alkynes catalyzed by the [PtHX(PR$_3$)$_2$]/[SnX$_2$] system ($PR_3 = PPh_3$, $PMePh_2$; X = Cl, Br) has been studied by means of *para*-hydrogen-induced polarization of ^{1}H-NMR spectra. Dihydride intermediates, confirming the stepwise hydrogenation at room temperature, were observed [46b].

Pt(II) complexes such as [PtCl$_2$(PPh$_3$)$_2$] and [PtHCl-(PPh$_3$)$_2$] are able to catalyze the hydromethoxycarbonylation of phenylacetylene according to Eq. (27) [47].



$$PhC{\equiv}CH + CO + CH_3OH \xrightarrow{PtHCl(PPh_3)_2} H_2C{=}C(Ph){-}C({=}O)OCH_3$$

(27)

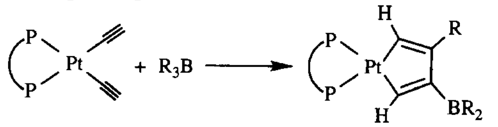


Scheme 11.

In particular, $[PtHCl(PPh_3)_2]$ displays the highest activity and a total regioselectivity towards the formation of α-methylene-benzeneacetate. The proposed mechanism involves the initial insertion of the alkyne into the Pt–H bond to give a σ-vinyl intermediate, followed by CO insertion giving an acylmetal complex, which, upon alcoholysis, afforded the carboxylic ester.

4.3.1.3. Pt–OH bonds, the hydration of alkynes. Treatment of $[PtCl_4]$ with CO at 40–110°C forms an efficient catalyst, $[HPtCl(CO)_2]$, for alkyne hydration to ketones [48a]. The proposed mechanism involves coordination of the alkyne and, in the presence of $HCl-H_2O$, the formation of a Pt–OH species, with subsequents insertion of the alkyne into the Pt–OH bond and formation of the enols similarly to what reported for the catalytic hydration of alkynes with the Zeise's dimer [48b].

4.3.1.4. Pt–B bond, the diboration of alkynes. Diethynyl platinum(II) complexes react with trialkylboranes to give platina-2,4-cyclopentadiene derivatives according to Eq. (28) [49a,b]:

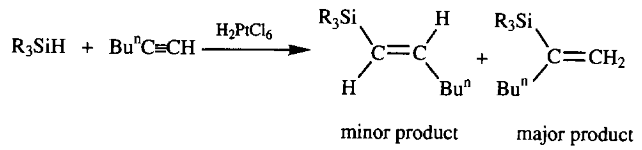


(28)

If substituents other than hydrogen are linked to the C≡C bond, the organoboration reaction is slow, yielding different products through the formation of a series of intermediates (Scheme 11) that can be detected by NMR spectroscopy [49c].

The reaction proceeds through the formation of the π-alkyne intermediate, which gave 1,1-organoboration forming complexes of the type **H**. This latter species undergoes an intramolecular rearrangement by migration of the 1-alkynyl group from platinum to boron giving intermediate species **I**, from which η^2-alkyne Pt(0) complexes **J** and/or η^3-alkenylboryl Pt(0) complexes **K** are obtained in a ratio that depends critically on the reaction conditions.

4.3.1.5. Pt–Si and Pt–Ge bonds, the hydrosilylation and hydrogermylation of alkynes. Alkynes can be hydrosilylated in the presence of chloroplatinic acid. The Markovnikov product is favored (Eq. (29)) [50]:



(29)

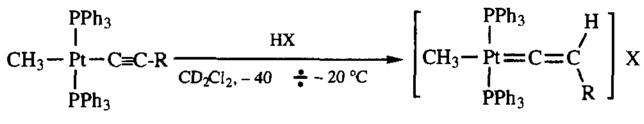
$[PtH(SiR_3)(PCy_3)_2]$ catalyzes the *cis* anti-Markovnikov addition of R_3SiH to EtC≡CH, PhC≡CH, MeC≡CMe, PhC≡CPh [50a]. Similarly, hydrogermylation of phenylacetylene occurs with H_2PtCl_6 and *cis*-$[PtCl_2(PPh_3)_2]$ with the formation of *trans*-$[R_3GeCH{=}CHPh]$ as the major product [50b].

4.3.1.6. P–C bonds. The reactivity of alkynyl complexes $Li_2[Pt(C{\equiv}CR)_4]$ and *cis*-$[Pt(C{\equiv}CR)_2(COD)]$ towards acidic phosphines PPh_2H and $PPh_2(O)H$ was recently described in order to establish if addition reaction of H–P could occur across the C≡C moiety to form P–C bonds [51]. No insertion reaction was observed, but the study demonstrated the possibility of preparing new alkynyl complexes containing secondary phosphines of the type $[Pt(C{\equiv}CR)_2(PPh_2H)_2]$ and very unusual tetralithium diplatinum species formed by a linear chain of four lithium ions sandwiched by two square-planar dianionic platinate units of the type $[\{Pt(C{\equiv}CR)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2\}_2]$ and $[\{Pt(C{\equiv}CR)(PPh_2O)_3Li_2(thf)(H_2O)\}_2]$ have been obtained.

4.3.2. Rearrangements and isomerization processes

4.3.2.1. Vinylidene intermediates. Vinylidene species have been reported for many transition metals and their chemistry has been recently reviewed [52]. Group 6–10 metal vinylidenes, which exhibit electrophilic properties, are involved in different catalytic reactions giving 2 + 2 cycloadditions, dimerization of alkynes, nucleophilic addition of alkynes and radical cycloaromatization [52].

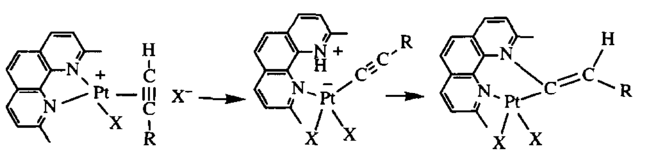
The intermediacy of a Pt(II)–vinylidene species, [Pt]=C=C(H)R, formed either by electrophilic attack of H^+ on a σ-bound acetylide or by the isomerization process of a coordinated η^2-terminal alkyne, was initially suggested by Chisholm and Clark in carbene formation by subsequent attack with MeOH [35], but only recently could vinylidene species be detected and spectroscopically characterized. A reactive Pt(II)–vinylidene species has been observed by multinuclear NMR techniques in the reaction of the acetylide complexes *trans*-$[Pt(Me)(C{\equiv}CR)(PPh_3)_2]$ (R = *p*-tolyl, Ph) with protic acids (Eq. (30)) [53]:



$HX = HBF_4{\cdot}Et_2O$, CF_3SO_3H; R = *p*-tolyl, Ph

(30)

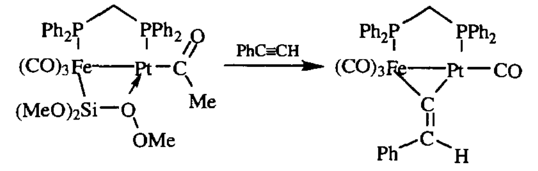
The ^{31}P-NMR spectra of the reaction mixture in CD_2Cl_2 at −40°C show the immediate quantitative formation of new species to which correspond singlets at ca. 30 ppm flanked by ^{195}Pt satellites ($^1J_{PPt}$ ca. 2800 Hz). The corresponding ^1H-NMR spectra show, together with signals attributed to new CH_3–Pt groups, broad singlets at ca. 4 ppm, flanked by ^{195}Pt satellites ($^3J_{HPt}$ ca. 40 Hz), attributed to the vinylidene proton. In good agreement are the spectroscopic data reported for the vinylidene complex $[PtX_2(Me_2phen)(=C=CHPh)]$ prepared according to Eq. (31) and for which an X-ray structure determination showed that the Pt and H atoms are in *trans* position, allowing a stabilization effect due to an interaction between the electrophilic vinylidene carbon and the N-atom of the phenanthroline ligand [54].



R = Ph, $CH_2CH_2CH_3$

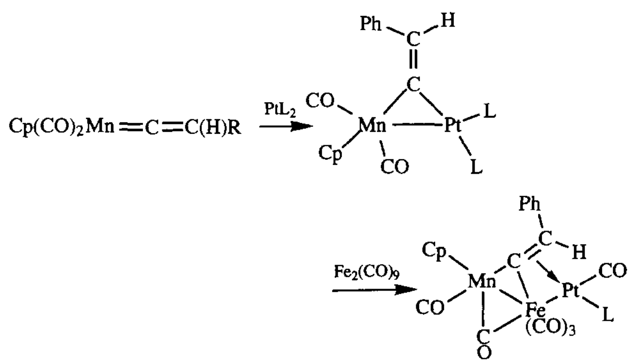
(31)

; A series of μ-vinylidene dinuclear Pt–M (M = Fe, Mn) species has been recently reported [55]. In the case of Pt–Fe the vinylidene complexes are formed by reacting the acyl complex $[(CO)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-}dppm)Pt\{C(O)Me\}]$ with an excess of phenylacetylene (Eq. (32)) [55a].



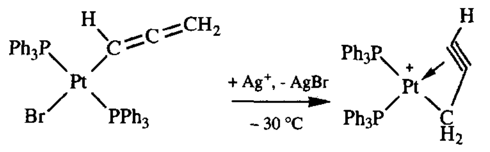
(32)

The dimetal vinylidene complexes $[Cp(CO)_2MnPt(\mu\text{-}C{=}C(H)Ph)L_2]$ ($L = PR_3$, $P(OR)_3$), which have been prepared by coupling of the mononuclear vinylidene derivative $[Cp(CO)_2Mn{=}C{=}C(H)Ph]$ with unsaturated PtL_2 species, react further with a $[Fe(CO)_4]$ moiety to form MnFePt trinuclear clusters containing μ^3-vinylidene moieties according to reaction (33) [55b,c,d]:



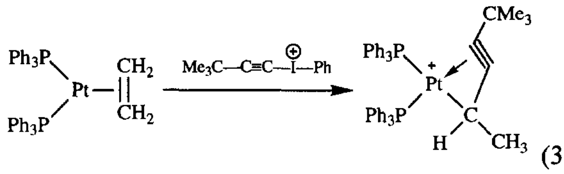
(33)

4.3.2.2. Allenyl/propargyl interconversion. π-Propargyl metal complexes, which are the triple-bond analogues of π-allyl complexes, can be obtained by different strategies [56]: (a) halide abstraction from σ-propargyl or σ-allenyl metal halide complexes [56b,c] (Eq. (34)):



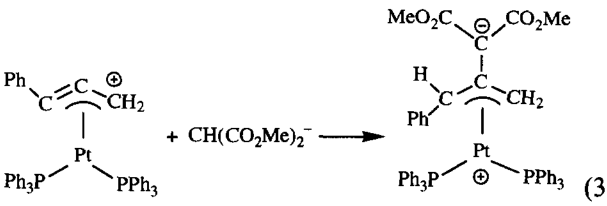
(34)

(b) rearrangements of η^1-homopropargyl metal complexes [56c,d] (Eq. (35)):



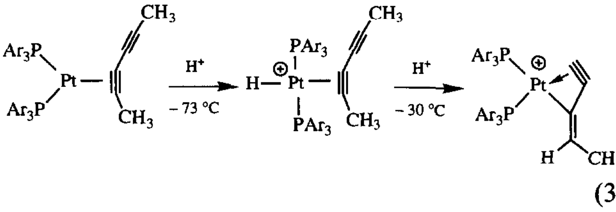
(35)

(c) reaction of π-propargyl intermediates with malonate nucleophiles as a route to zwitterionic trimethylmethane Pt and Pd complexes [56e] (Eq. (36)):



(36)

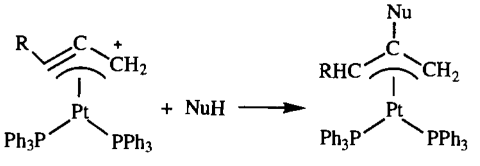
(d) protonation of diyne complexes at low temperature [56f] (Eq. (37)):



(37)

On the other hand, protonation of the eneyne complex $[Pt\{\eta^2\text{-}(HC{\equiv}CC(CH_3){=}CH_2\}(PPh_3)_2]$ produces the π-allyl derivative $[Pt\{\eta^3\text{-}(CH_2{=}CC(CH_3){=}CH_2\}(PPh_3)_2][BF_4]$ [56f].

The most relevant feature in the reactivity of η^3-propargyl complexes is the susceptibility to nucleophilic attack, which occurs at the central carbon atom affording the corresponding η^3-allyl complexes (Eq. (38)) [56a]:

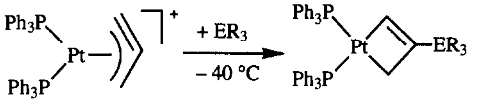


NuH = ROH, RNH_2, R_2NH, RSH (38)

It is noteworthy that only recently the nucleophilic attack at the central carbon has also been reported for (π-allyl)palladium complexes [57]; it proceeds only with σ-donor ligands such as TMEDA, TMPDA or bipy in the metal coordination sphere, whereas nucleophilic attack on the terminal carbon atom is the preferred reaction with π-acceptor ligands such as PPh_3, $P(OPh)_3$ or COD.

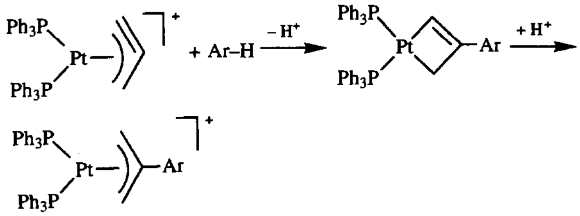
Approximate Fenske–Hall molecular orbital calculations [58] and density functional calculations suggest that the principal bonding interaction between Pt and the propargyl ligand occurs through the terminal carbon atoms of the ligand despite the observed short Pt–central carbon distance. The nucleophilic addition to the central carbon of the propargyl ligand is suggested to occur through a charge-controlled mechanism, assisted by the presentation of a low-lying acceptor orbital on the central carbon along the reaction path.

Attack of a nucleophile such as CO or CNR (R = *t*-Bu, CH_2Ph) to the metal center was observed in the reaction of $[Pt(\eta^3\text{-}CH_2C{\equiv}CPh)(PPh_3)_2]X$ (X = CF_3SO_3, BF_4, PF_6) to yield mixtures of the η^1-propargyl and allenyl complex *trans*-$[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(PPh_3)_2L]^+$ (L = CO, CNR) and *trans*-$[Pt(\eta^1\text{-}CPh{=}C{=}CH_2)(PPh_3)_2L]^+$, respectively [59]. The regioselective addition of NEt_3, PPh_3 or pyridine to the central carbon of the cationic η^3-propargyl/allenyl complex $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)][BF_4]$ leads to the formation of the new cationic platinacyclobutenes $[\overline{Pt\{CH_2C(Nu)CH\}}(PPh_3)_2][BF_4]$ (Nu = NEt_3, PPh_3, C_5H_5N) via formation of a C–N or C–P bond, respectively (Eq. (39)) [60]:



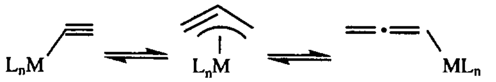
$ER_3 = NEt_3, PPh_3, NC_5H_5$ (39)

The electrophilicity of the central carbon in the η^3-C_3H_3 moiety of $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)]$ is so remarkable as to give regioselective addition of aromatic C–H-bonds, undergoing an organoplatinum induced electrophilic substitution leading to aryl vinylation according to reaction (40) [61]:



(40)

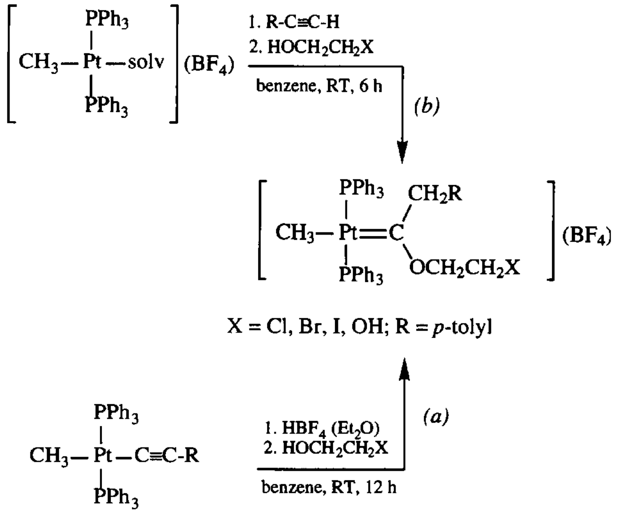
η^3-Propargyl species can be seen as key intermediates in the interconversion between η^1-propargyl and η^1-allenyl metal moieties, often postulated to take place in catalytic transformations [62a]:



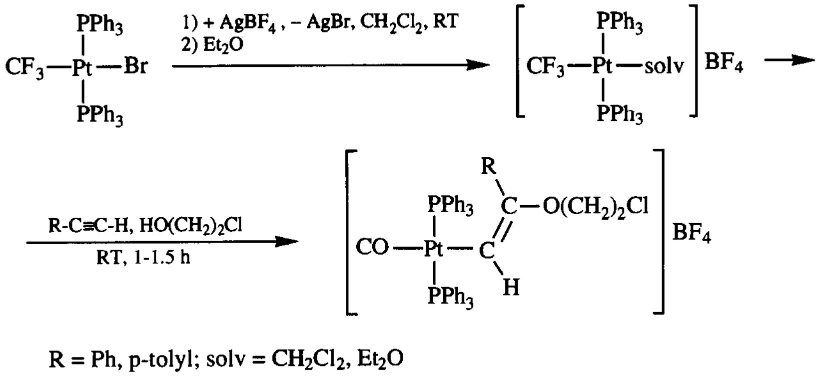
It is noteworthy that when heated in benzene, phenyl-substituted propargyl platinum(II) complexes of the type *trans*-$[Pt(CH_2C{\equiv}CPh)(X)(PPh_3)_2]$ (X = Cl, Br, I) [62] isomerize to the more stable allenyl isomers *trans*-$[Pt\{C(Ph){=}C{=}CH_2\}(X)(PPh_3)_2]$ to afford an equilibrium mixture (5:95 ratio), from which the allenyl complexes can be isolated as isomerically pure samples.

4.3.3. Nucleophilic attack

Alcohols are reported to react with alkynyl Pt(II) complexes to afford alkoxy(alkyl)carbene derivatives by a mechanism that is consistent with the intermediate formation of cationic metal–vinylidene complexes [35,63]. More recently, the reactivity of haloalcohols $HO(CH_2)_nX$ (*n* = 2,3; X = Cl, Br, I) with platinum(II)–alkynyl (Scheme 12, route (a)) and –alkyne complexes (Scheme 12, route (b)) to form the corresponding acyclic carbene derivatives has been reported [29a,c].

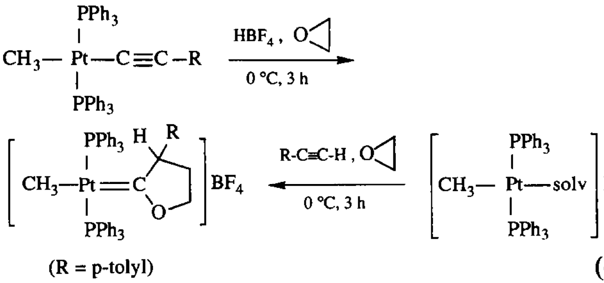


Scheme 12.



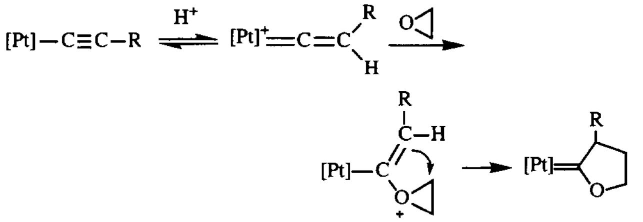
Scheme 13.

The reactions proceed without any evidence of cycloaddition products as otherwise observed for Pt(II)-coordinated CO [64a], RNC [64b] and RCN [64c] ligands to give cyclic carbenes or 2-oxazolines. However, cycloaddition reactions of oxirane to Pt(II)–alkynyl and –alkyne complexes yield cyclic oxycarbene derivatives (Eq. (41)) [29d]:

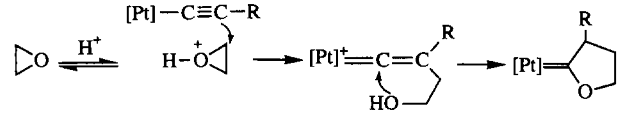


(41)

The proposed mechanism involves the formation of a vinylidene species via protonation of the acetylide ligand and subsequent nucleophilic attack by oxirane:



or initial protonation of oxirane and subsequent formation of a reactive hydroxyethyl vinylidene intermediate that undergoes intramolecular cyclization to the carbene species:

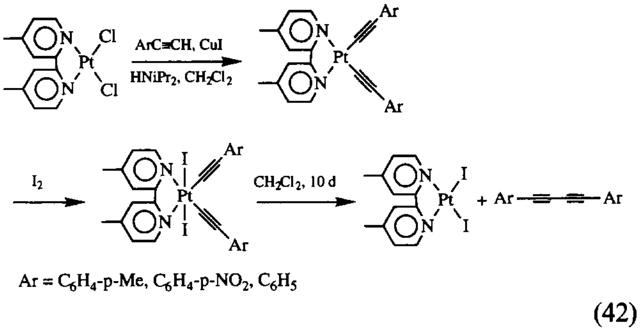


A different mechanism was proposed to explain the formation of β-alkoxyalkenyl derivatives in the reactions of the trifluoromethyl complexes *trans*-[Pt(CF$_3$)Br(PPh$_3$)$_2$] (R = *p*-tolyl, Ph) with alkynes and 2-chloroethanol in the presence of AgBF$_4$ [29b] (Scheme 13).

The higher electron-withdrawing properties of the CF$_3$ group compared with CH$_3$ would make the cationic complex [Pt(CF$_3$)(PPh$_3$)$_2$(solv)]$^+$ more electrophilic and this feature may reasonably explain a greater stabilization of the π-alkyne, which then undergoes nucleophilic attack by the alcohol at the β-carbon atom. In these reactions a CF$_3$ ligand is converted to CO as shown in the final complexes by a mechanism that involves electrophilic attack of H$^+$ on CF$_3$ to give a highly reactive intermediate difluorocarbene species, which rapidly hydrolyzed.

5. Pt(IV)–alkyne complexes

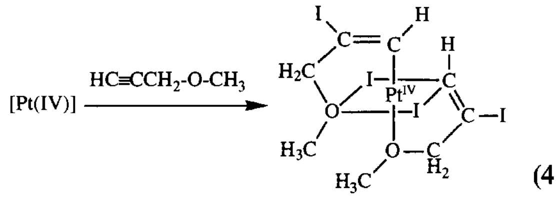
[Pt(Me$_2$bipy)Cl$_2$] (Me$_2$bipy = 4,4′-dimethyl-2,2′-bipyridine) and HC≡CAr react in the presence of diisopropylamine and CuI as catalyst to give the platinum(II) bis-acetylides [Pt(Me$_2$bipy)(C≡CAr)$_2$], which undergo oxidative addition of diiodine to afford quantitatively the Pt(IV) bis-acetylide complexes [Pt(Me$_2$bipy)(C≡CAr)$_2$(I)$_2$] according to reaction (42) [65a]:



(42)

The latter complex slowly reductively eliminates 1,4-di-*p*-tolyl-butadiyne with formation of [Pt(Me$_2$bipy)(I)$_2$].

Direct evidence was found that the catalytic conversion of alkynes to the diiodo-substituted dienes by the system Na$_2$PtCl$_6$–NaI–I$_2$ proceeds through a platinum(IV)–σ-vinyl complex. An essential feature of the alkynes is the presence of an oxygen atom that will interact with the metal center to form a neutral bicyclic complex (Eq. (43)) [65c]:

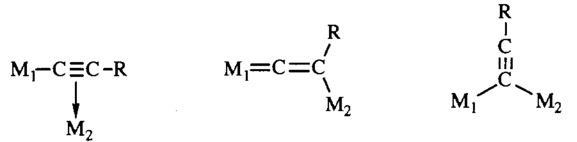


(43)

Extensive allenyl–propargyl interconversion has also been reported to occur at the platinum(IV) center in the complex $[PtMe_2(CH_2\text{-}C{\equiv}CMe)\{pz)_3BH\}]$ obtained by oxidative addition of $MeC{\equiv}CCH_2Br$ and $HC{\equiv}CCH_2Br$ to $[PtMe_2\{pz)_3BH\}]$ ($\{pz)_3BH\}$ = tris-pyrazol-1-yl borate) [65c].

6. Polynuclear complexes bearing C≡CR groups

The synthesis, structure and reactivity of a large number of homo- and heteropolynuclear complexes of platinum bearing μ-C≡CR groups as unique bridging ligands have been recently reviewed [66]. The structural features of the μ-C≡CR ligands can be described in terms of a resonance hybrid of the following three canonical structures:

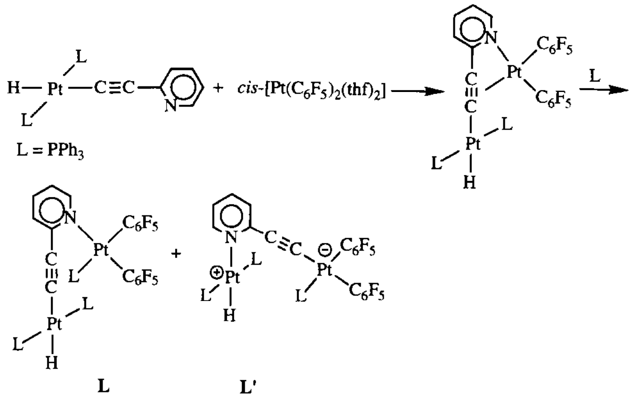


Thus, a series of heteropolynuclear Pt–Ag [67a–c], Pt–Cu [67a,c,68], Pt–Hg [69], Pt–Tl [70], Pt–Ru [71], Pt–Rh [72], Pt–Ir [73], Pt–Pt [74] and Pt–Pd [75] compounds has been prepared.

These studies are relevant in order to establish different synthetic routes to organometallic polymers with unusual physico-chemical properties, in particular for polymeric derivatives involving either σ- and π-alkyne moieties [67a,71c,73].

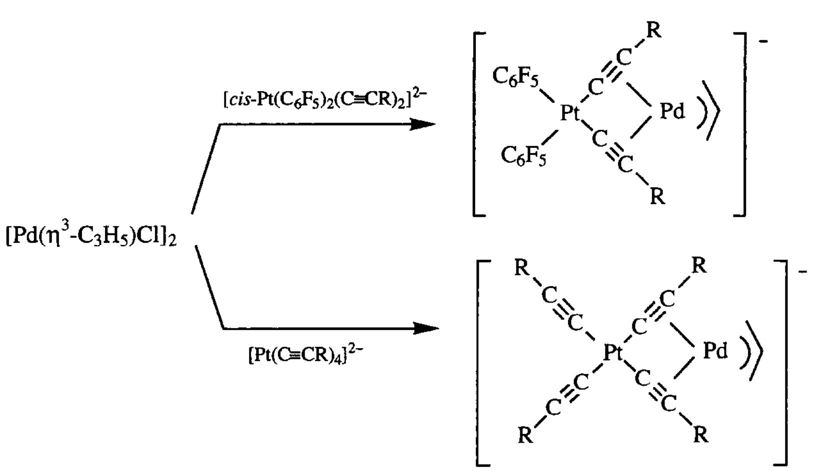
One of the most used strategy involves the reaction between mononuclear alkynyl complexes and a second substrate coordinatively unsaturated or a solvento complex. Thus, the reaction between *trans*-$[Pt(C{\equiv}CPh)H(PPh_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ [74b] gave the μ-phenylacetylene-bridged diplatinum complex $[(CO)_4(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2]$. The complex $[Pt(C{\equiv}CR)_4]^{2-}$ (R = *t*-Bu, $SiMe_3$) reacted with two equivalents of $[Rh(COD)(acetone)_2]^+$ to afford the neutral trinuclear adducts $[Pt(\mu\text{-}C{\equiv}CR)_4\{Rh(COD)\}_2]$; by further reaction of this latter complex with the dinuclear species $[Rh(\mu\text{-}X)(COD)]_2$ (X = Cl, OH) compounds of higher nuclearity of the type $[Pt(\mu\text{-}C{\equiv}CR)_4\{Rh_2(\mu\text{-}X)(COD)_2\}_2]$ can be obtained [72a]. Furthermore, *cis*-$[Pt(C_6F_5)_2(C{\equiv}CPh)_2](NBu_4)_2$ has been shown to react with the solvento species $[Cp^*M(PEt_3)(acetone)_2](ClO_4)_2$ (M = Rh, Ir) to give the bis-μ-alkynyl $[(PEt_3)Cp^*M(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (M = Rh, Ir) complexes [72b].

The compound *trans*-$[PtH(C{\equiv}CR)(PPh_3)]$ (R = 2-pyridyl) reacted with *cis*-$[Pt(C_6F_5)_2(tht)_2]$ in the presence of PPh_3 to afford a mixture of compounds of type L and L′ (Eq. (44)), while in the absence of added PPh_3 an unusual tetranuclear cluster is formed [74e]:



(44)

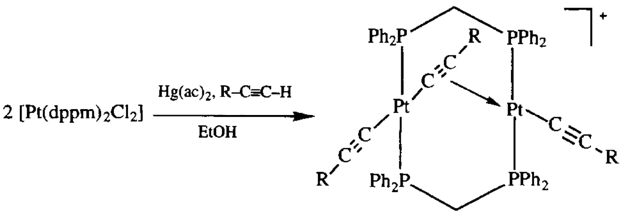
cis-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ and $[PtC{\equiv}CR)_4]^{2-}$ react with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ to give bis(μ-alkynyl) complexes via



Scheme 14.

halide displacement reactions according to Scheme 14 [75].

A series of A-frame diplatinum(II) acetylide complexes $[Pt_2(\mu\text{-dppm})_2(\mu\text{-C}\equiv CR)(C\equiv CR)_2]^+$ (R = alkyl, aryl) has been isolated and shown to exhibit strong luminescence both in the solid state and in solution [76] having long-lived (in the microsecond range) excited states. A general synthetic method to this type of complexes has been proposed [76c] involving deprotonation of phenylacetylene by mercury(II) acetate to form the corresponding mercury phenylacetylide which subsequently reacts with $[Pt(dppm)_2Cl_2]$ in refluxing ethanol according to reaction (45):



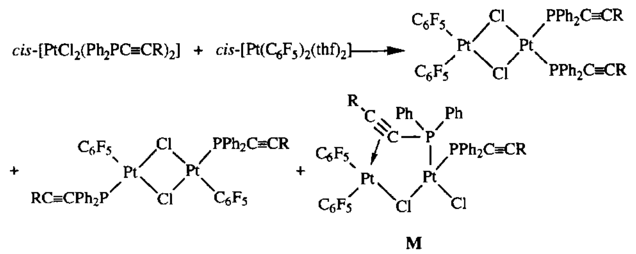
$R = C_6H_4\text{-p-OMe}, C_6H_4\text{-p-Et}; C_6H_4\text{-p-OEt}; Ph, Bu^t$

(45)

These A-frame acetylide complexes exhibit fluxional properties involving processes such as σ,π-acetylide exchange and a pseudoboat inversion with very small activation energy. These latter complexes exhibit a broad emission band centered at 570–650 nm. At 77 K the emission bands become intensified and narrower in fluid solutions and in the solid state. The spectra indicate the involvement of the π*(C≡CR) orbital in the transition.

In order to modify the physical properties of the acetylide complexes, N-donor ligands have been introduced in mixed metal alkynyl complexes of the type $[(t\text{-Bu}_2bipy)Pt(C\equiv CR)_2M(SCN)]$ (M = Cu, Ag; R = aryl, $SiMe_3$) [77]. Electrochemical studies on the Pt–Cu complexes revealed reversible reductive and irreversible oxidation processes occurring on the bipirydyl ligand and the Cu center, respectively.

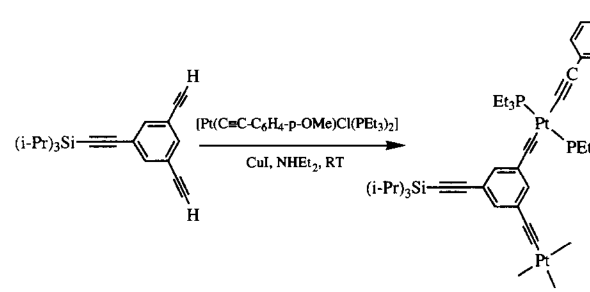
Homo- and heteropolynuclear complexes of palladium and platinum containing bridged phosphinoacetylene have been prepared as an alternative route to acetylide complexes. Phosphinoacetylenes of the type $PR_2C\equiv CR'$ (R,R′ = alkyl, aryl) can give different types of coordination modes involving the P atom, the C≡C system or they can act as bidentate ligands. Thus, by reacting *cis*-$[PtCl_2(PPh_2C\equiv CR)_2]$ (R = Ph, *t*-Bu) with *cis*-$[Pt(C_6F_5)_2(tht)_2]$ three types of products have been obtained: asymmetric homo dinuclear complexes, symmetric *trans* dinuclear derivatives and the unusual chlorine and diphenylphosphinoacetylene bridged compounds **M** (Eq. (46)) [78].



(46)

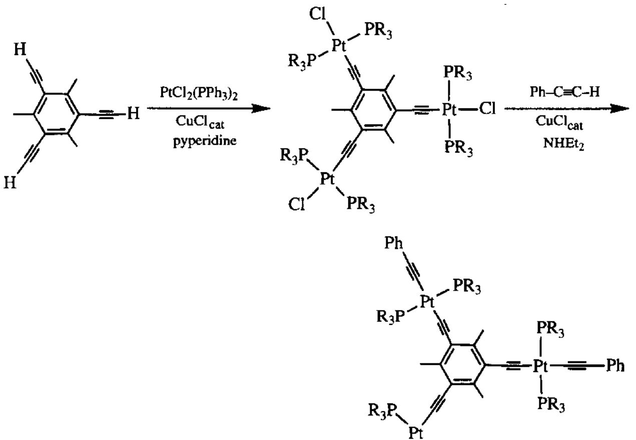
6.1. Organometallic dendrimers with Pt–C≡C– units

There is an increasing interest in the development of new strategies to synthesize well-defined nanosize macromolecules with specific functions. In this frame, dendrimers have a regularly branched architecture and spherical dimensions to be suitable starting compounds for new materials. Metal–acetylide dendrimers may have potential applicability as new materials since some platinum acetylides show unique properties and polymers exhibit a 2D-polyhexagonal graphite-like arrangement. Different synthetic strategies to dendrimers have been described. One of the most recent starts from 1,3,5-triethynylbenzene building blocks and uses trialkylsilyl protecting groups of the terminal acetylene (Eq. (47)) [79].



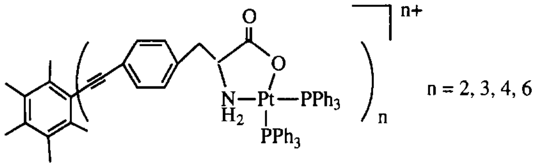
(47)

On the other hand, to the 1,3,5-triethynylbenzene skeleton platinum centers can be introduced by reaction with $[PtCl_2(PR_3)_2]$, which can further react with a terminal alkyne to afford the final products (Eq. (48)) [79c]:



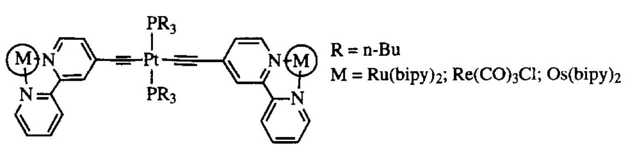
(48)

Recently, platinum–alkynyl bis, tris, *tetra*, hexapodal dendrimers of the type **N** have been prepared starting from the corresponding bis, tris, tetra, hexa ethynyl phenylalanines acting as *N*,*O*-chelate ligands [79d].



N

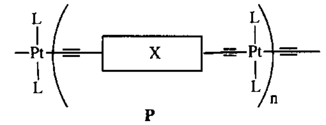
Some polynuclear systems that exhibit a rigid array around the platinum center can be related to dendrimers. These systems have a core of the type *trans*-[Pt$(PR_3)_2$$(C\equiv CY)_2$], where Y is a chelating ligand, tipically pyridine, bipyridine or terpyridine, able to give complexation with redox and/or photo-active metals such as [Ru$(bipy)_2$], [Os$(bipy)_2$] or [Re$(CO)_3$Cl] to form compounds of the type **O** [80].



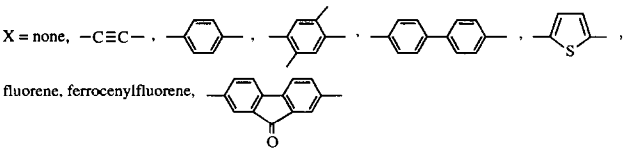
O

6.2. Organometallic polymers with Pt–C≡C– units

In recent years great interest has been attracted by polymeric structures that incorporate metals into the skeleton giving materials with different characteristics and physical properties such as liquid crystallinity, electroluminescence and photorefraction from conventional carbon-based polymers [81a]. In this context, bridging alkyne ligands appear of relevant importance due to their possibility to give σ- and π-bonds, a fluxional behavior [81b] and they appear to be precursors of naked C_n units [81c]. Typical platinum–acetylide polymers exhibit the **P** frame structure:



P



where L is a trialkylphosphine, in most cases *n*-Bu (to improve solubility in common solvents), Me or pyridyl-4-alkyl-substituted [81d].

It is noteworthy that even if most of the spacer groups studied in detail consist of conductive groups, a wide variety of studies is in progress to extend the easy synthetic methodology to produce higher-order oligomers introducing suitable connectors able to minimize electron-transfer events to favor long-range through-space processes. The rigid arrangement around the Pt center [82] is evident in the tendency to form liquid-crystal (nematic) phases in trichloroethylene [83]. The magnetic anisotropy of the polymer is shown by the strong response to magnetic and electric perturbations, leading to either parallel or perpendicular alignment with respect to the applied field [81a].

The optical properties of polymers of this type have been investigated as a function of chain length and the nature of space groups. Further extension of the π-conjugation has a significant effect, lowering energies for optical transitions and red shift [84]. Non-linear fluorescence and transmission have been studied at 595, 455, 532 and 513 nm. Pt–ethynyl compounds behave as broad-band optical limiters in the visible over a large range of pulse lengths from picoseconds to hundreds of nanoseconds [84c]. Oligonuclear and polynuclear alkynyl–platinum(II) complexes exhibit luminescence [85] attributed to a spin-forbidden Pt_2-to-alkyne charge-transfer transition.

Non-linear optical properties have been reported for platinum poly(yne)s showing large hyperpolarizabilities comparable to those of inorganic semiconductors such as InSb and Ge [86a].

Finally, of relevant interest appear some poly(yne) polymers that are optically active owing to the presence of chiral acetylene bridges [87a] and able to maintain a stable single-handed helical conformation as observed in the case of polymers obtained by insertion of isocyanides into the Pt–C≡C–Pt chain, which induces a screw-sense-selective polymerization [87b].

Acknowledgements

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References

[1] (a) R. Nast, Coord. Chem. Rev. 47 (1982) 89. (b) J.L. Davidson, in: P.S. Braterman (Ed.), Reactions of Coordinated Ligands, vol. 1, Plenum, New York, 1986, p. 825. (c) H. Werner, J. Organomet. Chem. 475 (1994) 45.

[2] (a) F.R. Hartley, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 6, Pergamon, Oxford, 1982, p. 691. (b) G.K. Anderson, in: F.G.A. Stone, E.W. Abel, G.Wilkinson and R.J. Puddephatt (Eds.), Comprehensive Organometallic Chemistry, vol. 9, Pergamon, Oxford, 1995, p. 490. (c) G. Brent Young, in: F.G.A. Stone, E.W. Abel, G.Wilkinson and R.J. Puddephatt (Eds.), Comprehensive Organometallic Chemistry, vol. 9, Pergamon, Oxford, 1995, p. 533.

[3] (a) J. Manna, K.D. John, H.D. Hopkins, Adv. Organomet. Chem. 38 (1995) 79. (b) J.N. Louwen, R. Hengelmolen, D.M. Grove, A. Oskam, R.L. Dekock, Organometallics 3 (1984) 908. (c) H. Masai, K. Sonogashira, H. Hagihara, Bull. Chem. Soc. Jpn. 44 (1971) 2226.

[4] G. Marinelli, W.E. Streib, J.C. Huffman, K.G. Caulton, M.R. Gagné, J. Takats, M. Dartineguave, C. Chardin, S.A. Jackson, O. Eisenstein, Polyhedron 9 (1990) 1867.

[5] F.P. Fanizzi, G. Natile, M. Lanfranchi, A. Tiripicchio, G. Pacchioni, Inorg. Chim. Acta 275 (1998) 500.

[6] (a) F.G.A. Stone, Acc. Chem. Res. 14 (1981) 318. (b) M.A. Bennett, E. Wenger, Chem. Ber. Recueil 130 (1997) 1029.

[7] (a) S.M. Davis, G.A. Somorijai, in: D.A. King, D.P. Woodruff (Eds.), The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, vol. 4, Elsevier, New York, 1982, p. 217.(b) J. Kua, W.A. Goddard III, J. Phys. Chem. 102 (1998) 9481.(c) J. Kua, W.A. Goddard III, J. Phys. Chem. 102 (1998) 9492.

[8] M. Green, D.M. Grove, J.A.K. Howard, J.L. Spencer, F.G.A. Stone, J. Chem. Soc. Chem. Commun. (1976) 759.

[9] D. Walther, T. Klettke, A. Schmidt, H. Gorls, W. Imhof, Organometallics 15 (1996) 2314.

[10] (a) Z. Lu, K.A. Abboud, W.M. Jones, J. Am. Chem. Soc. 114 (1992) 10991. (b) J. Klosin, K.A. Abboud, W.M. Jones, Organometallics 14 (1995) 2892. (c) Z. Lu, K.A. Abboud, W.M. Jones, Organometallics 12 (1993) 1471.

[11] M.A. Bennett, T. Dirnberger, D.C.R. Hockless, E. Wenger, A.C. Willis, J. Chem. Soc. Dalton. Trans. (1998) 271

[12] S. Shimada, M. Tanaka, K. Honda, Inorg. Chim. Acta 265 (1997) 1.

[13] (a) K. Sunkel, U. Birk, C. Robl, Organometallics 13 (1994) 1679. (b) K. Sunkel, U. Birk, Polyhedron 16 (1997) 3333.

[14] M.A. Bennett, H.P. Schwemlein, Angew. Chem. Int. Ed. Engl. 28 (1989) 1296.

[15] J. Klosin, K.A. Abboud, W.M. Jones, Organometallics 15 (1996) 596.

[16] L.B. Han, M. Tanaka, Chem. Commun. (Cambridge) (1999) 395.

[17] (a) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, Organometallics 15 (1996) 713. (b) G. Lesley, P. Nguyen, N.J. Taylor, T.B. Marder, A.J. Scott, W. Clegg, N.C. Norman, Organometallics 15 (1996) 5137.(c) C.N. Iverson, M.R. Smith III, Organometallics 15 (1996) 5155. (d) Q. Cui, D.G. Musaev, K. Morokuma, Organometallics 16 (1997) 1355. (e) L. Biao Han, M. Tanaka, J. Am. Chem. Soc. 120 (1998) 8249.

[18] M. Herberhold, U. Steffl, B. Wrackmeyer, J. Organomet. Chem. 577 (1999) 76.

[19] (a) M. Suginome, H. Nakamura, Y. Ito, Angew. Chem. Int. Ed. Engl. 36 (1997) 2516. (b) M. Suginome, T. Matsuda, H. Nakamura, Y. Ito, Tetrahedron 55 (1999) 8787.

[20] A.M. Caporusso, S. Barontini, P. Pertici, G. Vitulli, P. Salvadori, J. Organomet. Chem. 564 (1998) 57.

[21] S. Shimada, Y. Uchimaru, M. Tanaka, Chem. Lett. (1995) 223.

[22] A. Naka, T. Okada, A. Kunai, M. Ishikawa, J. Organomet. Chem. 547 (1997) 149.

[23] S. Klages, A.B. Permin, V.S. Petrosyan, J. Bargon, J. Organomet. Chem. 545 (1997) 201.

[24] T. Yasuda, A. Fukuoka, M. Hirano, S. Komiya, Chem. Lett. (1998) 29.

[25] Y. Koie, S. Shinoda, Y. Saito, B.J. Fitzgerald, C.P. Pierpont, Inorg. Chem. 19 (1980) 770.

[26] M.A. Bennett, D.E. Berry, T. Dirnberger, D.C.R. Hockless, E. Wenger, J. Chem. Soc. Dalton Trans. (1998) 2367.

[27] M.H. Chisholm, H.C. Clark, Inorg. Chem. 10 (1971) 2557.

[28] I. Ara, J.R. Berenguer, J. Fornies, E. Lalinde, M.T. Moreno, Organometallics 15 (1996) 1820.

[29] (a) U. Belluco, R. Bertani, R.A. Michelin, M. Mozzon, F. Benetollo, G. Bombieri, R.J. Angelici, Inorg. Chim. Acta 240 (1995) 567. (b) R.A. Michelin, M. Mozzon, B.Vialetto, R. Bertani, G. Bandoli, R.J. Angelici, Organometallics 17 (1998) 1220. (c) U. Belluco, R. Bertani, S. Fornasiero, R.A. Michelin, M. Mozzon, Inorg. Chim. Acta 275 (1998) 515.(d) R.A. Michelin, M. Mozzon, B. Vialetto, R. Bertani, F. Benetollo, G. Bombieri, R.J. Angelici, Organometallics 15 (1996) 4096.

[30] (a) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, H. Hagihara, J. Organomet. Chem. 145 (1978) 101. (b) A. Sebald, C. Stader, B. Wrackmeyer, W. Bensch, J. Organomet. Chem. 311 (1986) 233. (c) R.J. Cross, M.F. Davidson, J. Chem. Soc. Dalton Trans. (1986) 1987.

[31] B.W. Davies, R.J. Puddephatt, N.C. Payne, Can. J. Chem. 50 (1972) 2276.

[32] (a) D. Steinborn, M. Tschoerner, A. von Zweidorf, J. Sieler, H. Bogel, Inorg. Chim. Acta 234 (1995) 47. (b) M. Gerisch, F.W. Einemann, H. Bogel, D. Steinborn, J. Organomet. Chem. 548 (1997) 247.

[33] H.C. Clark, L.E. Manzer, J. Am. Chem. Soc. 95 (1973) 3812.

[34] F. Canziani, L. Garlaschelli, M.C. Malatesta, J. Organomet. Chem. 146 (1978) 179.

[35] M.H. Chisholm, H.C. Clark, Acc. Chem. Res. (1973) 202.

[36] (a) M.H. Chisholm, H.C. Clark, J. Am. Chem. Soc. 94 (1972) 1532.(b) M.H. Chisholm, H.C. Clark, J. Chem. Soc. Chem. Commun. (1971) 1484.

[37] H. Nakai, S. Fukuda, H. Nakatsuji, J. Phys. Chem. A 101 (1997) 973.

[38] D. Steinborn, S. Becke, C. Bruhn, F.W. Heinemann, J. Organomet. Chem. 556 (1998) 189.

[39] M.B. Dinger, W. Henderson, J. Chem. Soc. Dalton Trans. (1998) 1763.

[40] A.C. Dema, C.M. Lukehart, Inorg. Chim. Acta 264 (1997) 193.

[41] F. Ozawa, T. Hikida, Organometallics 15 (1996) 4501.

[42] (a) A.J. Canty, H. Jin, J.D. Penny, J. Organomet. Chem. 573 (1999) 30. (b) F. Ozawa, J. Kamite, Organometallics 17 (1998) 5630.

[43] (a) H.C. Clark, R.J. Puddephatt, Inorg. Chem. 9 (1970) 2670. (b) H.C. Clark, R.J. Puddephatt, Inorg. Chem. 10 (1971) 18.

[44] (a) T.G. Appleton, H.C. Clark, R.J. Puddephatt, Inorg. Chem. 11 (1972) 2074. (b) H.C. Clark, L.E. Manzer, J. Organomet. Chem. 101 (1975) 347. (c) H.C. Clark, L.E. Manzer, Inorg. Chem. 13 (1974) 1291.

[45] A. Furlani, I. Collamati, G. Sartori, J. Organomet. Chem. 17 (1969) 463.

[46] (a) R.D. Cramer, E.L. Jenner, R.V. Lindsey, U.G. Stolberg, J. Am. Chem. Soc. 85 (1963) 1691. (b) C. Deibele, A.D. Permin, V.S. Petrosyan, J. Bargon, Eur. J. Inorg. Chem. (1998) 1915.

[47] A. Scrivanti, G. Menchi, U. Matteoli, J. Mol. Catal. A: Chem. 96 (1995) 223.

[48] (a) W. Hiscox, P.W. Jennings, J. Am. Chem. Soc. (1990) 7333. (b) W. Baidossi, M. Lahav, J. Blum, J. Org. Chem. 62 (1997) 669.

[49] (a) A. Sebald, B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (1983) 1293. (b) A. Sebald, B. Wrackmeyer, J. Organomet. Chem. 304 (1986) 271. (c) B. Wrackmeyer, A. Sebald, J. Organomet. Chem. 544 (1997) 105.

[50] (a) M. Ciriano, M. Green, J.A.K. Howard, M. Murray, J.L. Spencer, F.G.A. Stone, C.A. Tsipis, Adv. Chem. Ser. 167 (1978) 111. (b) R.J.P. Corriu, J.J.E. Moreau, J. Organomet. Chem. 40 (1972) 73.

[51] L.R. Falvello, J. Fornies, J. Gomez, E. Lalinde, A. Martin, M.T. Moreno, J. Sacristan, Chem. Eur. J. 5 (1999) 474.

[52] C. Bruneau, P.H. Dixneuf, Acc. Chem. Res. 32 (1999) 311.

[53] U. Belluco, R. Bertani, F. Meneghetti, R.A. Michelin, M. Mozzon, J. Organomet. Chem. 583 (1999) 131.

[54] F.P. Fanizzi, C. Pacifico, M. Lanfranchi, A. Tiripicchio, G. Bandoli, G. Pacchioni, G. Natile, Proceedings IV Co.G.I.C.O., Udine, Italy, 1998, C17.

[55] (a) M. Knorr, C. Strohmann, P. Braunstein, Organometallics, 15 (1996) 5653. (b) A.B. Antonova, A.A. Johansson, N.A. Deykhina, A.G. Ginzburg, E.D. Korniyets, S.V. Kovalenko, N.I. Pavlenko, P.V. Petrovskii, A.I. Rubaylo, I.A. Sukhina, Inorg. Chim. Acta 230 (1995) 97. (c) A.B. Antonova, A.A. Johansson, N.A. Deykhina, E.D. Kornyiets, N.I. Pavlenko, G.V. Burmakina, A.I. Rubaylo, A.G. Ginzburg, P.V. Petrovskii, J. Organomet. Chem. 524 (1996) 81. (d) A.B. Antonova, A.A. Johansson, N.A. Deykhina, D.A. Pogrebnyakov, N.I. Pavlenko, A.I. Rubaylo, F.M. Dolgushin, P.V. Petrovskii, A.G. Ginzburg, J. Organomet. Chem. 577 (1999) 238.

[56] (a) C.P. Casey, A.D. Selmeczy, J.R. Nash, C.S. Yi, D.R. Powell, R.K. Hayashi, J. Am. Chem. Soc. 118 (1996) 6698. (b) T.M. Huang, R.H. Hsu, C.S. Yang, J.T. Chen, G.H. Lee, Y. Wang, W. Yu, Organometallics 13 (1994) 3657. (c) M.W. Baize, P.W. Blosser, V. Plantevin, D.G. Schimpff, J.C. Gallucci, A. Wojcicki, Organometallics 15 (1996) 164. (d) P.J. Stang, C.M. Crittel, A.M. Arif, Organometallics 12 (1993) 4799. (e) V. Plantevin, P.W. Blosser, J.G. Gallucci, A. Wojcicki, Organometallics 13 (1994) 3651. (f) C.P. Casey, S. Chung, Y. Ha, D.R. Powell, Inorg. Chim. Acta 265 (1997) 127.

[57] A. Aranyos, K.J. Szabo, A.M. Castano, J.E. Backvall, Organometallics 16 (1997) 1058.

[58] J.P. Graham, A. Wojcicki, B.E. Bursten, Organometallics 18 (1999) 837.

[59] (a) P.W. Blosser, D.G. Schimpff, J.C. Gallucci, A. Wojcicki, Organometallics 12 (1993) 1993. (b) M.N. Ackermann, R.K. Ajmera, H.E. Barnes, J.C. Gallucci, A. Wojcicki, Organometallics 18 (1999) 787.

[60] Y.C. Cheng, Y.K. Chen, T.M. Huang, C.I. Yu, G.H. Lee, Y. Wang, J.T. Chen, Organometallics 17 (1998) 2953.

[61] J.T. Chen, R.H. Hsu, A.J. Chen, J. Am. Chem. Soc. 120 (1998) 3243.

[62] (a) J. Tsuji, T. Mandai, Angew. Chem. Int. Ed. Engl. 34 (1995) 2589. (b) S. Ogoshi, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, Inorg. Chim. Acta 265 (1997) 9.

[63] M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem. 22 (1983) 59.

[64] (a) L. Zanotto, R. Bertani, R.A. Michelin, Inorg. Chem. 29 (1990) 3265. (b) R. Bertani, M. Mozzon, F. Benetollo, G. Bombieri, R.A. Michelin, J. Chem. Soc. Dalton Trans. (1990) 1197. (c) R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R.J. Angelici, Organometallics 13 (1994) 1341.

[65] (a) S.L. James, M. Younus, P.R. Raithby, J. Lewis, J. Organomet. Chem. 543 (1997) 233. (b) V. Amanikov, S.A. Mitchenko, I.P. Beletskaya, S.E. Nefedov, I.L. Eremenko, Inorg. Chem. Commun. 1 (1998) 411. (c) A.J. Canty, H. Jin, J.D. Penny, J. Organomet. Chem. 573 (1999) 30.

[66] J. Fornies, E. Lalinde, J. Chem. Soc. Dalton Trans. (1996) 2587.

[67] (a) S. Yamazaki, A.S.Deeming, D.M. Speel, D.E. Hibbs, M.B. Hursthouse, K.M. AbdulMalik, Chem. Commun. (Cambridge) (1997) 177. (b) I. Ara, J.R. Berenguer, J. Fornies, E. Lalinde, M.T. Moreno, J. Organomet. Chem. 510 (1996) 63. (c) J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, J. Organomet. Chem. 490 (1995) 179. (d) I. Ara, J. Fornies, E. Lalinde, M.T. Moreno, M. Tomas, J. Chem. Soc. Dalton Trans. (1995) 2397.

[68] S. Yamazaki, A.J. Deeming, M.B. Hursthouse, K.M. AbdulMalik, Inorg. Chim. Acta 235 (1995) 147.

[69] J.R. Berenguer, J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, J. Chem. Soc. Dalton Trans. (1994) 3343.

[70] I. Ara, J.R. Berenguer, J. Fornies, J. Gomez, E. Lalinde, R.I. Merino, Inorg. Chem. 36 (1997) 6461.

[71] (a) M. Sato, E. Mogi, J. Organomet. Chem. 508 (1996) 159. (b) L.J. Farrugia, N. MacDonald, R.D. Peacock, Polyhedron 17 (1998) 2877. (c) M. Younus, N.J. Long, P.R. Raithby, J. Lewis, J. Organomet. Chem. 570 (1998) 55.

[72] (a) I. Ara, J.R. Berenguer, J. Fornies, E. Lalinde, Organometallics 16 (1997) 3921. (b) I. Ara, J.R. Berenguer, E. Eguizabal, J. Fornies, E. Lalinde, A. Martin, F. Martinez, Organometallics 17 (1998) 4578.

[73] J.R. Berenguer, J. Fornies, E. Lalinde, F. Martinez, J. Chem. Soc. Chem. Commun. (1995) 1227.

[74] (a) J.R. Berenguer, J. Fornies, E. Lalinde, F. Martinez, Organometallics 14 (1995) 2532. (b) I. Ara, J.R. Berenguer, J. Fornies, E. Lalinde, M. Tomas, Organometallics 15 (1996) 1014. (c) I. Ara, L.R. Falvello, J. Fornies, E. Lalinde, A. Martin, F. Martinez, M.T. Moreno, Organometallics 16 (1997) 5392. (d) G.J. Spivak, R.J. Puddephatt, J. Organomet. Chem. 551 (1998) 383. (e) J.R. Berenguer, E. Eguizabal, L.R. Falvello, J. Fornies, E. Lalinde, A. Martin, Organometallics 18 (1999) 1653. (f) L.R. Falvello, S. Fernandez, J. Fornies, E. Lalinde, F. Martinez, M.T. Moreno, Organometallics 16 (1997) 1326.

[75] J.R. Berenguer, J. Fornies, E. Lalinde, F. Martinez, Organometallics 15 (1996) 4537.

[76] (a) V.V.W. Yam, L.P. Chan, T.F. Lai, Organometallics 12 (1993) 2197. (b) T. Tanase, H. Ukaji, T. Igoshi, Y. Yamamoto, Inorg. Chem. 35 (1996) 4114. (c) W.W.V. Yam, P.K.Y. Yeung, L.P. Chan, W.M. Kwok, D.L. Phillips, K.L. Yu, R.W.K. Wong, H. Yan, Q.J. Meng, Organometallics 17 (1998) 2590.

[77] C.J. Adams, P.R. Raithby, J. Organomet. Chem. 578 (1999) 178.

[78] J. Fornies, E. Lalinde, A. Martin, M.T. Moreno, A.J. Welch, J. Chem. Soc. Dalton Trans. (1995) 1333.

[79] (a) K. Onitsuka, M. Fujimoto, N. Ohshiro, S. Takahashi, Angew. Chem. Int. Ed. Engl. 38 (1999) 689. (b) S. Leininger, P.J. Stang, S. Huang, Organometallics 17 (1998) 3981. (c) N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, J. Organomet. Chem. 569 (1998) 195. (d) B. Kayser, J. Altman, H. Noth, J. Knizek, W. Beck, Eur. J. Inorg. Chem. (1998) 1791.

[80] (a) M. Hissler, R. Ziessel, J. Chem. Soc. Dalton Trans. (1995) 893. (b) A. Harriman, M. Hissler, R. Ziesslel, A. De Cian, J. Fischer, J. Chem. Soc. Dalton Trans. (1995) 4067. (c) A. Harrimann, R. Ziessel, Coord. Chem. Rev 171 (1998) 331.

[81] (a) P. Nguyen, P. Gomez-Elipe, I. Manners, Chem. Rev. 99 (1999) 1515. (b) W. Beck, B. Niemer, M. Wieser, Angew. Chem. Int. Ed. Engl. 32 (1993) 923. (c) H. Lang, Angew. Chem. Int. Ed. Engl. 33 (1994) 547. (d) C.J. Adams, S.L. James, P.R. Raithby, Chem. Commun. (Cambridge) (1997) 2155.

[82] (a) J. Davy, M.E. Gunter, E.R.T. Tiekink, Z. Kristallogr. 213 (1998) 483. (b) R.D. Markwell, I.S. Butler, A.K. Kakkar, M.S. Khan, Z.H. Al-Zakwani, J. Lewis, Organometallics 15 (1996) 2331.

[83] (a) S. Takahashi, E. Murata, M. Kariya, K. Sonogashira, N. Hagihara, Macromolecules 12 (1979) 1016. (b) S. Takahashi, H. Morimoto, Y. Takai, K. Sonogashira, N. Hagihara, Mol. Cryst. Liq. Crystallogr. 72 (1981) 101.

[84] (a) W.Y. Wong, W.K. Wong, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1998) 2761. (b) J. Lewis, P.R. Raithby, W.Y. Wong, J. Organomet. Chem. 556 (1998) 219. (c) J. Lewis, N.J. Long, P.R. Raithby, G.P. Shields, W.Y. Wong, M. Younus, J. Chem. Soc. Dalton Trans. (1997) 4283. (d) N. Chawdhury, A. Kohler, R.H. Friend, W.Y. Wong, J. Lewis, M. Younus, P.R. Raithby, T.C. Corcoran, M.R.A. Al-Mandhary, M.S. Khan, J. Chem. Phys. 110 (1999) 4963. (e) K. Onitsuka, N. Ose, F. Ozawa, S. Takahashi, J. Organomet. Chem. 578 (1999) 169.

[85] V.W.W. Yam, K.K.W. Lo, K.M.C. Wong, J. Organomet. Chem. 578 (1999) 3.

[86] (a) S. Guha, K. Kang, P.L. Porter, J.F. Roach, D.E. Remy, F.J. Aranda, D.V.G.L.N. Rao, Opt. Lett. 17 (1992) 264. (b) T.J. McKay, J.A. Bolger, J. Staromlynska, J.R. Davy, J. Chem. Phys. 108 (1998) 5537. (c) J. Staromlynska, T.J. McKay, J.A. Bolger, J.R. Davy, J. Opt. Soc. Am. B 15 (1998) 1731.

[87] (a) K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, Chem. Commun. (Cambridge) (1998) 643. (b) F. Takei, K. Yanai, K. Onitsuka, S. Takahashi, Angew. Chem. Int. Ed. Engl. 35 (1996) 1554.