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Platinum(IV) hydride chemistry

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This article is dedicated to Professor Barry Lever on the occasion of his 65th birthday

Contents

Abstract

A review is given for hydridoplatinum(IV) chemistry, especially in organometallic derivatives. It treats, both directly characterized complexes and those that are proposed as short-lived reaction intermediates. The complexes are of current interest as potential intermediates in C–H activation reactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydridoplatinum(IV) chemistry; C–H activation reactions; Organometallic derivatives

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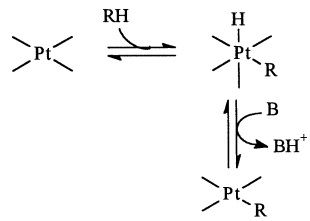
1. Introduction

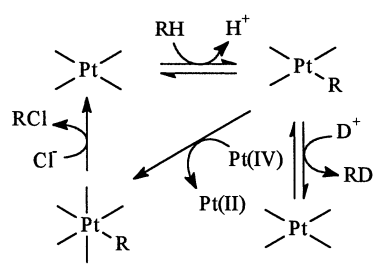
The activation of alkanes by platinum(II) complexes was discovered in 1969 by Shilov, shortly after the analogous activation of arenes, and is suggested to occur according to Scheme 1. It can lead to simple H–D exchange or to oxidation of alkanes to alcohols or alkyl halides [1,2].

There has been much interest recently in this chemistry, both in terms of developing useful catalysis [3] and in terms of understanding the mechanisms of catalysis in greater detail [1,2]. One of the likely mechanisms for the C–H activation step is oxidative addition to platinum(II) to give a transient alkyl(hydrido)platinum(IV) intermediate as shown in Eq. (1) [1–3].

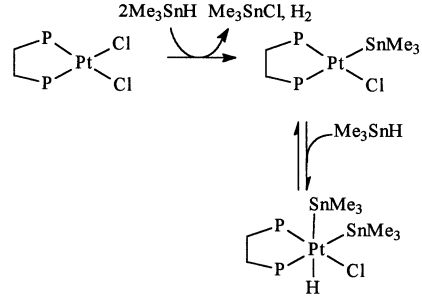


(1)

In this context, it appears timely to give a brief review of the chemistry of platinum(IV) hydride complexes, especially as it is relevant to C–H bond activation. Platinum(II) hydrides were first prepared by Chatt and Shaw in 1957 [4] and have been studied in great detail in the intervening years [5], but platinum(IV) hydrides are less well known. Chatt and Shaw also reported the reversible addition of HCl to *trans*-$[PtHCl(PEt_3)_2]$ to give $[PtH_2Cl_2(PEt_3)_2]$, the first platinum(IV) hydride, which was characterized by elemental analysis and IR but which evolved HCl easily on heating [4]. Some other early examples of platinum(IV) hydrides were prepared from Group 14 hydrides by oxidative addition to platinum(II) [6,7]. A typical reaction to form a stannyl(hydrido)platinum(IV) complex is shown in Eq. (2) ($PP = Ph_2PCH_2CH_2PPh_2$) [7], and some complexes containing germyl(hydrido)platinum(IV) units are shown in Chart 1 [6]. More recent syntheses of silyl(hydrido)platinum(IV) complexes are shown in Eqs. (2b) and (2c) [8]. Such compounds could be involved in dehydrooligomerization of silanes, in hydrosilation of unsaturated compounds or in silyl exchange reactions [8] Eq. (2d).



Scheme 1.



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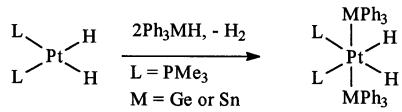

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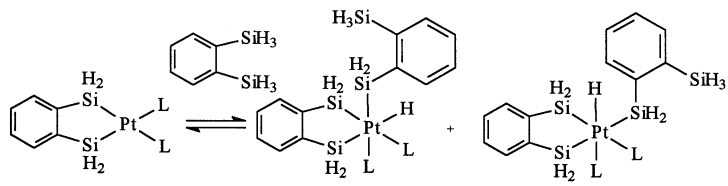

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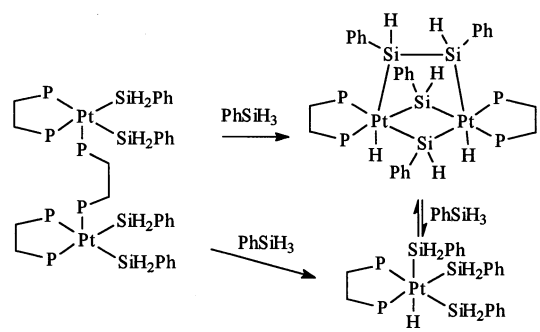

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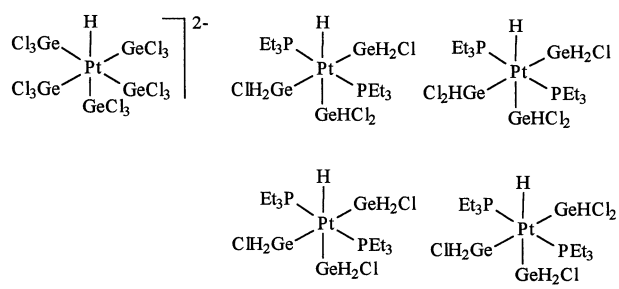
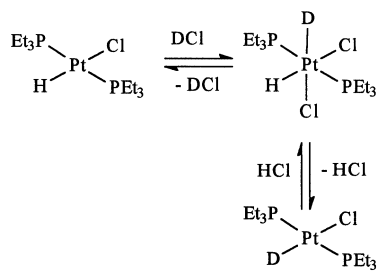


Chart 1.

The simplest platinum(IV) hydride is the salt $Na_2[PtH_6]$, whose structure has been reported recently [9]. This review will focus on the synthesis and reactivity of platinum(IV) hydride complexes containing two- or three-hydride ligands or, especially, containing both hydride and σ-bonded organic groups.

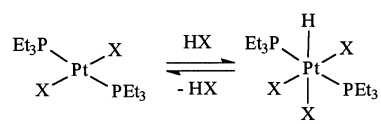
2. Hydrido-, dihydrido- and trihydridoplatinum(IV) complexes

The reversible addition of HCl to *trans*-$[PtHCl(PEt_3)_2]$ to give $[PtH_2Cl_2(PEt_3)_2]$ was confirmed by kinetic studies of H–D exchange using DCl/D_2O, as depicted in Eq. (3) [10].



(3)

The equilibria were then studied in detail using NMR techniques by Ebsworth et al. [11–13]. Some typical NMR data are listed in Table 1. The equilibrium shown in Eq. (4) was fast at room temperature, and hydride formation was preferred in the sequence $X = I > Br \gg Cl$. The primary oxidative addition was shown to be *trans*, as shown in Eq. (5), though this was then followed by halogen scrambling in mixed complexes $[PtHXY_2(PEt_3)_2]$, X, Y = halogen or X = halogen, Y = cyanide.



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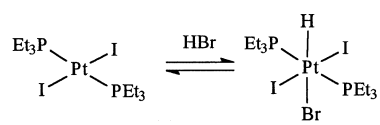

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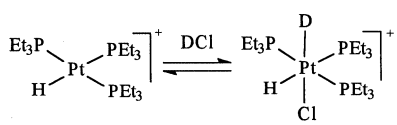


(6)

In principle, the monohydridoplatinum(IV) complexes could also be prepared from *trans*-$[PtHX(PEt_3)_2]$ and X_2, but these reactions usually gave mixtures of $[PtH_2X_2(PEt_3)_2]$ and $[PtX_4(PEt_3)_2]$ as major products. The *trans*-oxidative addition

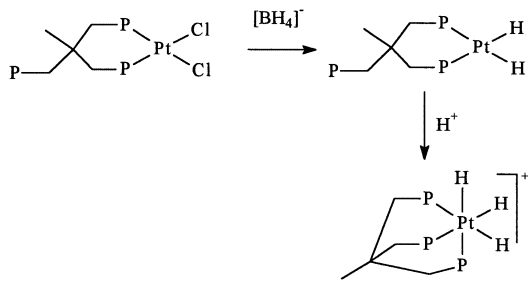
Table 1
^{1}H-NMR data for hydridoplatinum(IV) complexes and some hydridoplatinum(II) complexes for comparison

Complex	δ(PtH)	^1J(PtH)	*trans*-Atom
trans-[PtH(P^{t}Bu$_3$)$_2$]$^+$	−36.5	2605	None
trans-[PtH(CH$_2$Cl$_2$)(P^{i}Pr$_3$)$_2$]$^+$	−22.8	1852	Cl
trans-[PtHCl(PEt$_3$)$_2$]	−16.8	1275	Cl
trans-[PtHBr(PEt$_3$)$_2$]	−15.5	1331	Br
trans-[PtHI(PEt$_3$)$_2$]	−12.6	1369	I
trans-[PtHBr$_3$(PEt$_3$)$_2$]	−18.3	845	Br
trans-[PtHI$_3$(PEt$_3$)$_2$]	−16.4	784	I
cis-*cis*-*trans*-[PtH$_2$Cl$_2$(PEt$_3$)$_2$]	−18.2	1176	Cl
cis-*cis*-*trans*-[PtH$_2$Br$_2$(PEt$_3$)$_2$]	−16.9	1204	Br
cis-*cis*-*trans*-[PtH$_2$I$_2$(PEt$_3$)$_2$]	−15.0	1186	I
cis-*cis*-*trans*-[PtH$_2$Cl(CN)(Pet$_3$)$_2$]	−12.3	706	CN
	−18.4	1225	Cl
cis-*cis*-*trans*-[PtH$_2$Br(CN)(PEt$_3$)$_2$]	−12.6	695	CN
	−17.3	1210	Br
cis-*cis*-*trans*-[PtH$_2$I(CN)(PEt$_3$)$_2$]	−13.3	661	CN
	−15.8	1232	I
cis-*mer*-[PtH$_2$Cl(PEt$_3$)$_3$]$^+$	−17.1	1107	Cl
	−10.1	710	P
trans-[PtH(H$_2$)(PCy$_3$)$_2$]$^+$	−10.4	1445	H$_2$
	(−0.3, H$_2$)	295	H
cis-*cis*-*trans*-[PtH$_2$Cl$_2$(PCy$_3$)$_2$]	−18.8	1125	Cl
cis-*cis*-*trans*-[PtH$_2$Br$_2$(PCy$_3$)$_2$]	−17.6	1145	Br
cis-*cis*-*trans*-[PtH$_2$I$_2$(PCy$_3$)$_2$]	−15.8	1115	I
fac-PtH$_3${MeC(CH$_2$PPh$_2$)$_3$}]$^+$	−9.4	929	P
[PtH$_2$(SiEt$_3$)Tp′]	−20.1	1178	N
[PtH$_3$Tp′]	−20.0	1169	N

was also expected in reactions of DX with *trans*-[PtHX(PEt$_3$)$_2$] but halogen scrambling was very fast when X = Y = halogen, so the stereochemistry of addition could not be proved. The *trans*-addition was proved in the reaction of DCl with [PtH(PEt$_3$)$_3$]$^+$ to give [PtHDCl(PEt$_3$)$_3$]$^+$, as shown in Eq. (6).

Similar reactions occur when *trans*-[PtHX(PR$_3$)$_2$] reacts with HX to give [PtH$_2$X$_2$(PR$_3$)$_2$], where R = Cy and X = halogen [14]. However, reaction of H[BAr$_4$] with *trans*-[PtHCl(PR$_3$)$_2$] occurs by protonation of chloride to give HCl and *trans*-[PtH(solv)(PR$_3$)$_2$]$^+$, when Ar = 3,5-C$_6$H$_3$(CF$_3$)$_2$ and R = Cy or *t*-Bu [14–16], and reaction with *trans*-[PtH(CN)(PR$_3$)$_2$] gives the HNC complex *trans*-[PtH(CNH)(PR$_3$)$_2$]$^+$ by protonation of cyanide. Finally, H[BAr$_4$] reacts with *trans*-[PtHR(PR$_3$)$_2$] with R = H, Me, Ph or SiH$_3$ at the hydride ligand to give the dihydrogen complexes of platinum(II) *trans*-[PtR(H$_2$)(PR$_3$)$_2$]$^+$ [14,16,17]. Hence, there are three established modes of reaction of protic acids HY with platinum(II) hydrides *trans*-[PtHX(PR$_3$)$_2$], as summarized in Scheme 2, arising from protonation at Pt, X or H [14–17]. In general, the products of Scheme 2 are thermodynamically controlled and it is possible that unobserved intermediates are formed by kinetic control.

The first trihydridoplatinum(IV) complex appears to be *fac*-$PtH_3[\{MeC(CH_2PPh_2)_3\}]^+$ which is formed by reaction of $[PtCl_2\{\eta^2\text{-}MeC(CH_2PPh_2)_3\}]$ with $Na[BH_4]$ in methanol, perhaps by protonation of the intermediate $[PtH_2\{\eta^2\text{-}MeC(CH_2PPh_2)_3\}]$ by methanol (Eq. (7)) [18]. The complex $[PtH_3Tp']$, $Tp' = HB(N_2C_3HMe_2)_3$, is formed by the reaction sequence shown in Eq. (7b), and the intermediate $[PtH_2(SiEt_3)Tp']$ has been structurally characterized [18].



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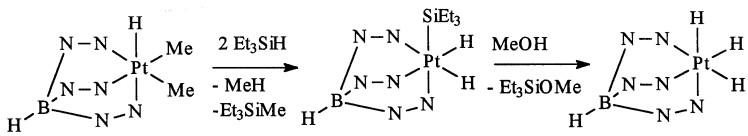
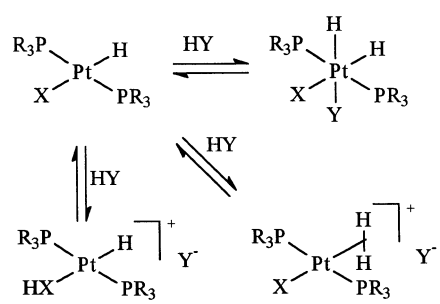


(7b)

3. Platinum(II) complexes with 3c–4e X — H···Pt bonds

There are several platinum(II) complexes, especially in orthometallated compounds, in which an N–H, O–H or C–H bond undergoes a secondary bonding interaction with platinum. Some of these are shown in Chart 2, and the NMR data for compounds **1**–**6** are given in Table 2 [19–23]. The interaction is thought to be formed by donation from the filled d_{x^2} orbital of platinum(II) to the hydrogen atom and is structurally characterized by a roughly linear Pt···H — X grouping. The strongest interactions occur (Table 2) when the hydrogen has most acidic character,



Scheme 2.

Table 2
NMR data for platinum(II) complexes with E-H···Pt bonds

Complex	δ(Pt···H)	^1J(PtH)
$[Pt(C_6F_5)_3(NC_9H_6OH)]^-$, **1**	12.2	69
$[Pt(C_6F_5)_3(NC_9H_6Me)]^-$, **2**	4.1	0
$[Pt(C_6F_5)_3(NC_{13}H_9)]^-$, **3**	13.4	22
$[PtBr(C_{10}H_6NMe_2)(C_{10}H_6Nme_2H)]$, **4**	15.8	180
$[PtBr(C_6H_4CH_2Nme_2)(C_6H_4CH_2NMe_2H)]$, **5**	11.3	72
$[PtCl_2(PMe_3)(NC_9H_6Me)]$, **6**	4.0	12

i.e. for $^+$NH···Pt > OH···Pt > CH···Pt [23]. In fact, there is structural evidence that the CH···Pt interaction may be repulsive [23]. The compounds of Chart 2 can be considered to lie on the reaction coordinate which would lead to X–H oxidative addition, if that were thermodynamically favored. Compounds **1**–**5** are therefore on the way to aryl(hydrido)platinum(IV) compounds.

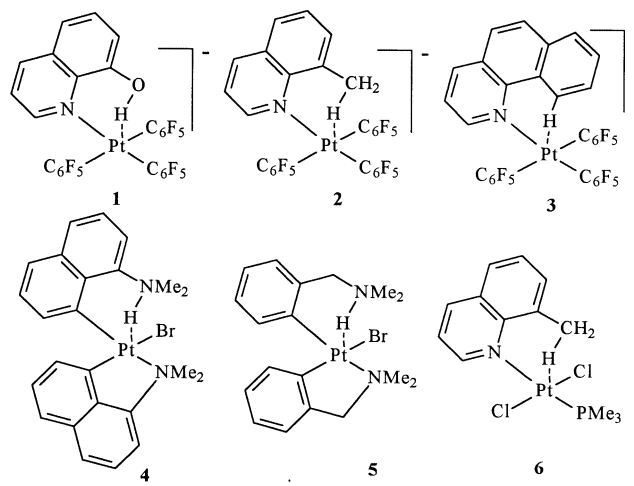
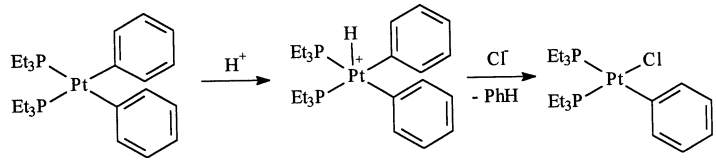


Chart 2.

4. Compounds formed by protonation of organoplatinum(II) complexes

Alkyl- and aryl(hydrido)platinum(IV) complexes were first proposed as reaction intermediates in the cleavage of arylplatinum(II) bonds by acids, such as in the reaction of *cis*-$[PtPh_2(PEt_3)_2]$ with HCl to give *cis*-$[PtClPh(PEt_3)_2]$ and PhCl [24,25]. However, at that time, the intermediates were not directly detected. Kinetic studies did not distinguish clearly between the oxidative addition/reductive elimination mechanism and a direct electrophilic substitution mechanism, shown in simplified form in Eqs. (8) and (9), respectively. Arguments for and against each mechanism were made based on kinetics, isotope effects and other factors [24,25].



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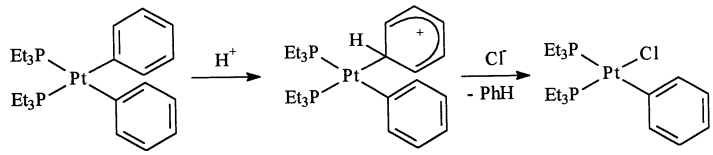
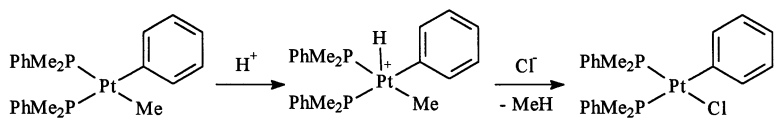
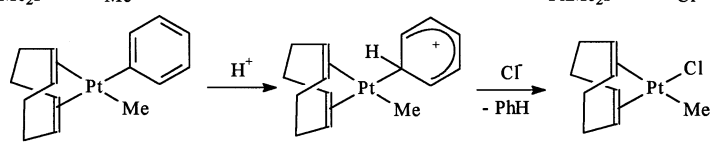


(9)

One approach to distinguish between the mechanisms was to study the selectivity of reactions of methyl(aryl)platinum(II) complexes. It was suggested that the oxidative addition/reductive elimination mechanism would lead to cleavage of the methylplatinum(II) bond, whereas electrophilic attack at carbon would lead to cleavage of the arylplatinum(II) bond. There was a ligand dependence on selectivity as shown in Eqs. (10) and (11), with phosphine ligands promoting methyl cleavage and 1,5-*cyclo*-octadiene promoting phenyl cleavage [26]. Photoelectron spectra confirm that the σ-MePt and platinum 5d levels are close in energy [27], and so attack at either site by the proton may be affected by the nature of the supporting ligands. The HOMO is a σ-Pt-L orbital that is delocalized over both methyl and neutral ligands and is sterically shielded in some cases, whereas the Pt $5d_{z^2}$ orbital is localized and sterically accessible. It was proposed that stronger donors, such as phosphines or nitrogen donors, favor attack at platinum while weaker donors, such as alkenes, favor attack at carbon [26,27].



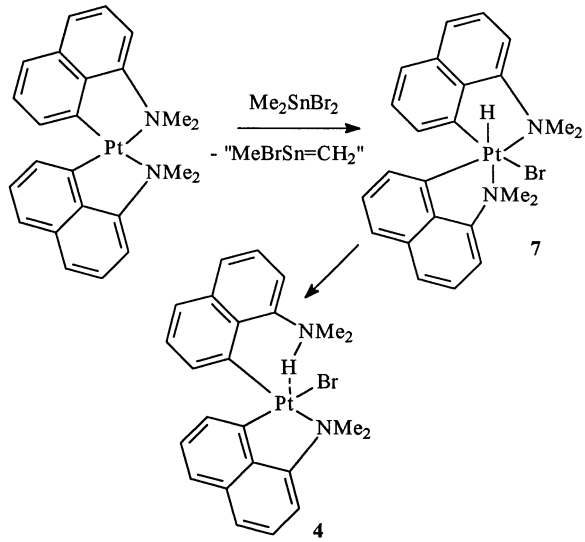
(10)



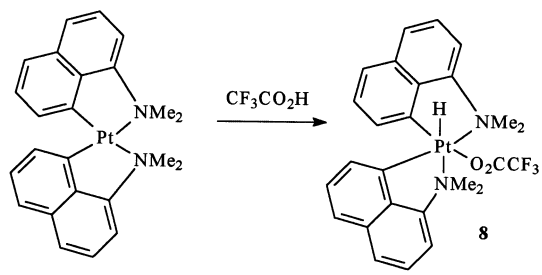
(11)

The first isolated aryl(hydrido)platinum(IV) complexes were prepared by reaction of organotin halides or protic acids with orthometalated arylplatinum(II) compounds. The hydrides could isomerize to the zwitterionic compounds such as **4** (Chart 2). An example, showing formation and tautomerism to **4** of the diaryl(hydrido)platinum(IV) complex **7**, is shown in Scheme 3, and the NMR data for selected hydrides are listed in Table 3 [23,28]. Note the dramatic difference in NMR properties of the hydrogen atom for **4** and **7** (Tables 2 and 3; **4**, $\delta(\text{Pt}\cdots\text{H}) = 15.8$, $^1J(\text{PtH}) = 180$ Hz; **7**, $\delta(\text{Pt–H}) = -20.3$, $^1J(\text{PtH}) = 1540$ Hz). The NMR technique thus allows easy characterization of the isomers, whose energies may be similar.

The direct reaction of the orthometalated platinum(II) complex with HX led to the zwitterionic complexes such as **4** when X = Cl or Br, but did give the hydride derivative **8** when $X = CF_3CO_2$ as shown in Eq. (12) [23,28].

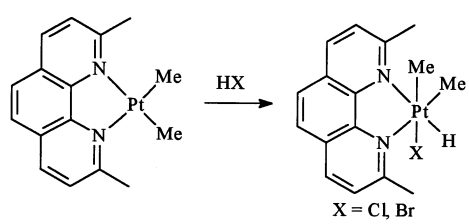


Scheme 3.



(12)

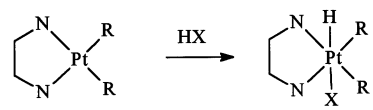
Diimine and diamine ligands give short-lived alkyl- or aryl(hydrido)platinum(IV) complexes by protonation as indicated in Eqs. (13–15). The complexes with the ligand 2,9-dimethyl-1,10-phenanthroline give *cis*-addition (Eq. (13)) [29], while other ligands give *trans*-addition (Eqs. (14 and 15)) [30,31]. The compounds easily decompose by reductive elimination with C–H bond formation to eliminate alkane or arene at temperatures $< 0°C$, so they could not be isolated [29–31]. Selected NMR data are given in Table 3.



(13)

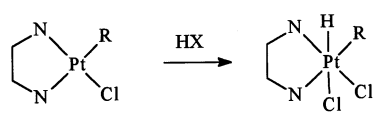
Table 3
NMR data for organo(hydrido)platinum(IV) complexes (abbreviations: Tp′ = $HB(N_2C_3HMe_2)_3$; Tp = $HB(N_2C_3H_3)_3$; Tp″ = $B(N_2C_3H_3)_4$; TACN = triazacyclononane; and dmm = dimethyl maleate)

Complex	δ(PtH)	^1J(PtH)	*trans*-atom
$[PtBrH(1\text{-}C_{10}H_6NMe_2)_2]$, **7**	−20.35	1540	N
$[Pt(O_2CCF_3)H(1\text{-}C_{10}H_6NMe_2)_2]$, **8**	−19.37	1610	N
cis-$[PtHClMe_2(dmphen)]$	−22.1	1404	N
trans-$[PtHClMe_2(tmeda)]$	−23.1	1726	Cl
$[PtHCl_2Me(tmeda)]$	−23.6	1292	Cl
$[PtHCl_2(CH_2Ph)(tmeda)]$	−23.9	1230	Cl
trans-$[PtHClMe_2(bu_2bipy)]$	−21.8	1590	Cl
trans-$[PtHBrMe_2(bu_2bipy)]$	−20.9	1630	Br
trans-$[PtHIMe_2(bu_2bipy)]$	−19.2	1655	I
$[PtHCl_2Me(PEt_3)_2]$	−18.8	1223	Cl
$[PtH(OTf)_2Me(PEt_3)_2]$	−25.6	1500	O
$[PtHMe_2Tp']$	−20.9	1358	N
$[PtHPh_2Tp']$	−18.9	1360	N
$[PtHMe_2Tp]$	−20.2	1358	N
$[PtHMe_2Tp']$	−20.1	1360	N
$[PtHMe_2(TACN)]^+$	−19.5	1339	N
$[PtHMe_2(BPMA)]^+$, **9**	−20.0	1384	N(py)
$[PtHMe_2(BPMA)]^+$, **10**	−19.0	1396	N(amine)
$[PtHMe_2(TPMA)]^+$, **11**	−20.1	1366	N(py)
$[PtHMe_2(TPMA)]^+$, **12**	−20.4	1462	N(amine)
$[PtHCl(COMe)_2(bipy)]$, **13**	−18.3	1566	N
$[PtHCl(COMe)_2(phen)]$, **14**	−18.1	1582	N
[PtHCl(dmm)(dmphen)], **15**	−25.7	1178	Cl
mer,*trans*-$[PtH_3Ph(PEt_3)_2]$, **16**	−9.5	701	H
	−13.2	598	C(Ph)
$[PtH_2Ph(SnMe_3)(Pet_3)_2]$, **17**	−11.3	780	P
	−14.0	535	H
$[PtH_2Ph(SnMe_3)(Pet_3)_2]$, **18**	−10.1	674	H
$[PtHMe_3(bu_2bipy)]$, **19**	−7.0	805	Me
$[(\mu\text{-}H)\{PtMe_3(bu_2bipy)\}_2]$, **20**	−11.7	442	Me
$[PtH_2(C_6H_4C_6H_4)(PEt_3)_2]$, **21**	−10.6	637	C(Ar)
$[PtH_2MeTp]$	−20.0	1276	N
[PtHMePhTp′]	−19.3	1368	N



NN = $Me_2NCH_2CH_2NMe_2$, R = Me or CH_2Ph, X = Cl
NN = 2,2′-bipyridine, R = Me, X = Cl
NN = 4,4′-Me_2bipy, R = Me, X = Cl
NN = 4,4′-Bu_2bipy, R = Me, X = Cl, Br or I

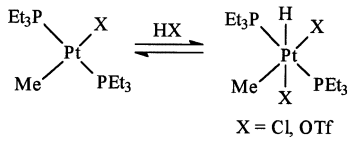
(14)



NN = $Me_2NCH_2CH_2NMe_2$, R = Me or CH_2Ph, X = Cl

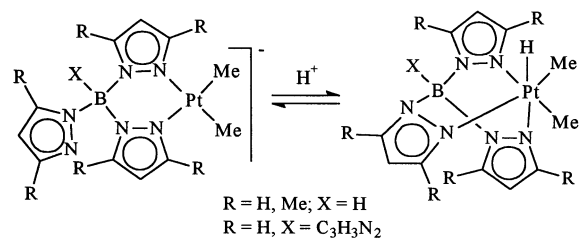
(15)

Hydrido(methyl)platinum(IV) complexes with triethylphosphine ligands have also been identified by low temperature NMR techniques (Eq. (16), Table 3) [30,32]. The formation of $[PtH(OTf)_2Me(PEt_3)_2]$ (Eq. (16)) is reversible in the temperature range from -80 to -40°C, and methane loss to give $[Pt(OTf)_2(PEt_3)_2]$ occurs at -20°C [32].

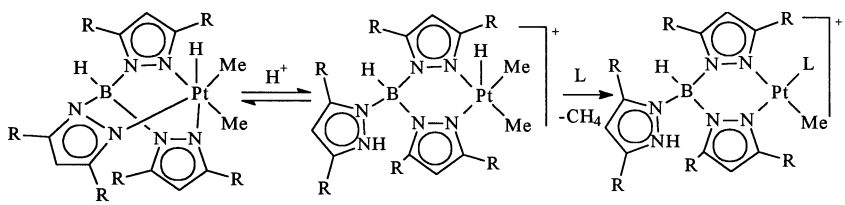


(16)

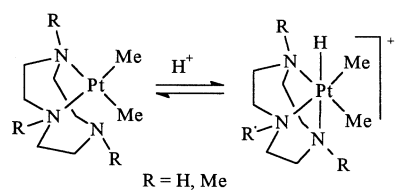
In all these cases, the reductive elimination of alkane or arene is believed to occur from a 5-coordinate hydridoplatinum(IV) intermediate formed by preliminary dissociation of an anionic ligand (halide, triflate) from the octahedral hydridoplatinum(IV) complexes shown in Eqs. (13-16) [29–32]. Very stable hydridoplatinum(IV) complexes were then prepared by using strongly coordinating *fac*-tridentate ligands, as illustrated in Eqs. (17 and 18) [33–35]. For these compounds there is no easy route to reductive elimination. The structures of the products of Eq. (17), R = Me, X = H, and Eq. (18), R = H (as the triflate salt) have been determined [33,35].



(17)



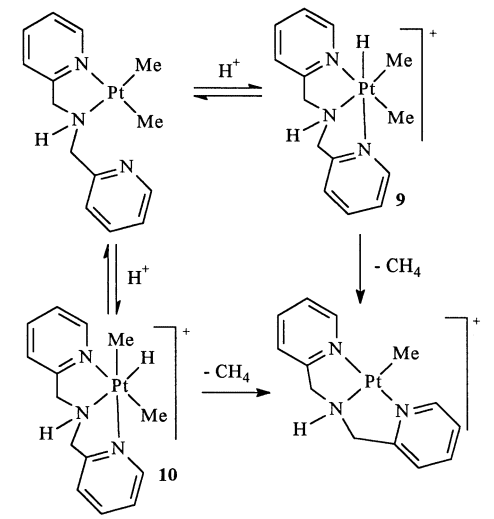
(17b)



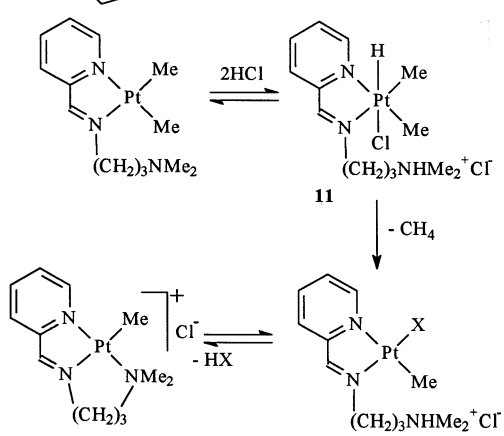
(18)

Only weak acids are needed for the protonation reactions, including phenol and acetic acid for Eq. (17) and even, reversibly, methanol for Eq. (18). The protonation can be reversed by addition of strong base, such as aqueous NaOH [33–35]. Excess

acid can accelerate the C–H reductive elimination by protonation of a ligand, leading to dissociation to the 5-coordinate intermediate from which the elimination occurs (Eq. (17b)) [33]. With more flexible tridentate ligands, compounds of intermediate thermal stability can be formed as illustrated in Eq. (19). Isomer **9** is formed first and then equilibrates with isomer **10**, before reductive elimination of methane occurs [36,37]. If the third nitrogen atom cannot easily coordinate, protonation of the free nitrogen atom occurs first and a second proton is needed to give the hydride as shown in Eq. (20). In this case, no stabilization of the hydride is observed and reductive elimination occurs at low temperature [38]. Free imine groups in dimethylplatinum(II) complexes are protonated in preference to the platinum atom and this can lead to the formation of aminoalkylplatinum(IV) complexes rather than hydridoplatinum(IV) complexes [38].



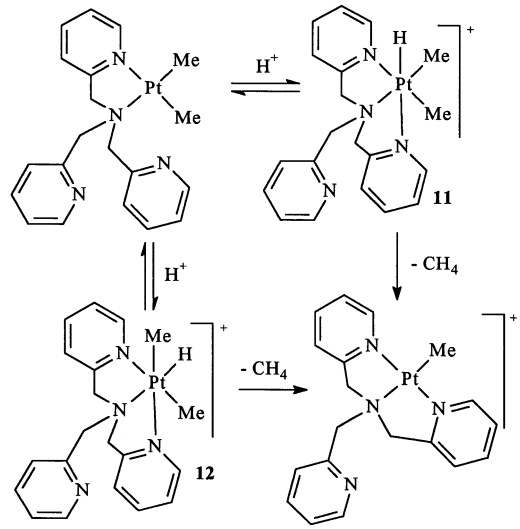
(19)



(20)

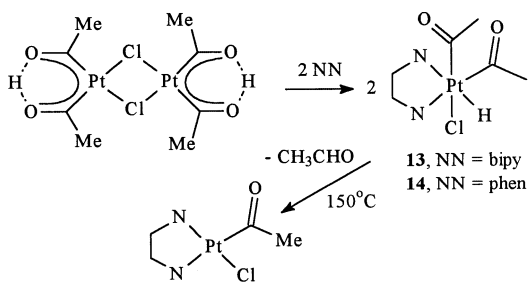
The presence of a fourth nitrogen donor has little effect on the stability of the hydridoplatinum(IV) complex but does lead to much faster isomerization between the isomeric complexes, **11** and **12** in Eq. (21) than between **9** and **10** in Eq. (19).

It is likely that the free pyridyl group can reversibly and easily deprotonate the initially formed complex **11** and so facilitate the isomerization [39].



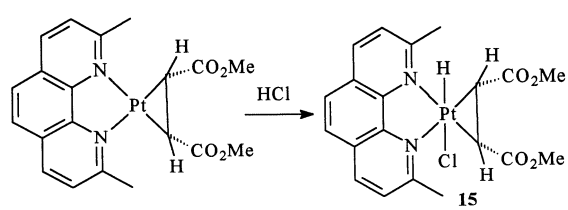
(21)

An interesting example of internal proton transfer has been observed to give stable hydrido(diacyl)platinum(IV) complexes as shown in Eq. (22). The products such as **13** and **14** have remarkable thermal stability and reductively eliminate acetaldehyde only on heating to about 150°C [40].



(22)

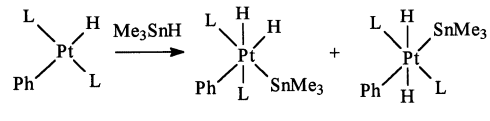
Finally, it is noted that the 5-coordinate hydridoplatinum(II) complexes [PtHX-(alkene)(2,9-dimethyl-1,10-phenanthroline)], formed by reaction of HX with [Pt(alkene)(2,9-dimethyl-1,10-phenanthroline)] as shown in Eq. (23) for complex **15**, have similar NMR properties as the octahedral hydridoplatinum(IV) complexes (Table 3) [41].



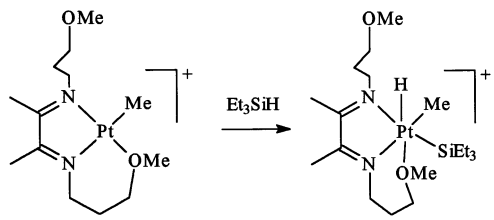
(23)

5. Compounds formed by reaction of organoplatinum complexes with metal hydrides

The reduction of the phenylplatinum(II) complex *trans*-$[PtPh(MeOH)L_2]^+$, L = PEt_3, with $NaBH_4$ gave *trans*-$[PtHPhL_2]$, but sometimes also *mer*,*trans*-$[PtH_3PhL_2]$, **16**, perhaps involving protonation at platinum by methanol as the oxidation step. Hydrido(phenyl)platinum(IV) complexes **17** and **18** were also prepared by oxidative addition of trimethylstannane to *trans*-$[PtHPhL_2]$, as shown in Eq. (24) [42]. These were the first aryl(hydrido)platinum(IV) complexes to be detected. A hydrido(methyl)silylplatinum(IV) complex has been prepared in a similar way as shown in Eq. (24b)[42].

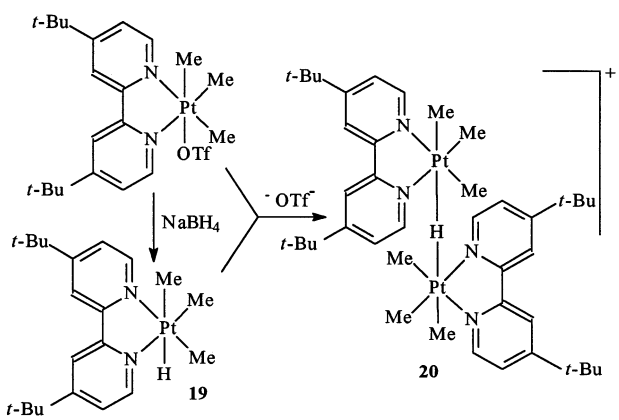


(24)

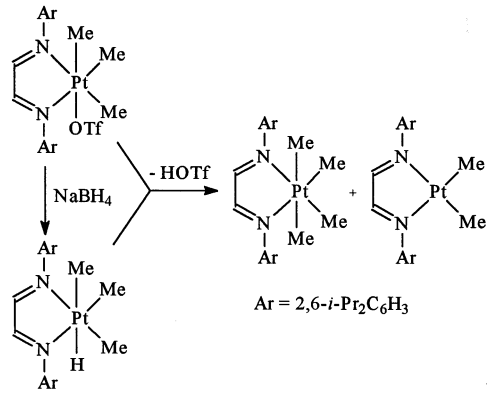


(24b)

Stable hydrido(trimethyl)platinum(IV) complexes have been prepared as shown in Eq. (25). The complex $[PtHMe_3(bu_2bipy)]$, **19**, is stable in solution as formed with excess hydride present, but it reacts with water easily to form the only known bridging hydridodiplatinum(IV) complex **20** [43]. Complex **20** that has been structurally characterized is also formed provided a stoichiometric amount of hydride is used as shown in Eq. (25). If bulkier ligands are used, the bridging hydride cannot form and methyl group transfer occurs instead as shown in Eq. (25b) [43].

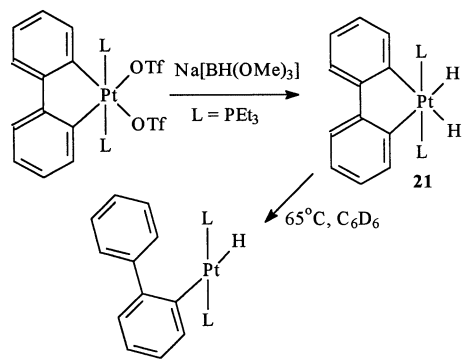


(25)



(25b)

A stable dihydridoplatinum(IV) complex **21** is formed from a biphenylene derived arylplatinum complex as shown in Eq. (26). It decomposes selectively by C–H reductive elimination to give a biphenylplatinum(II) complex. An isomer of **21** was proposed as an intermediate in the platinum complex catalyzed hydrogenation of biphenylene to biphenyl [44].



(26)

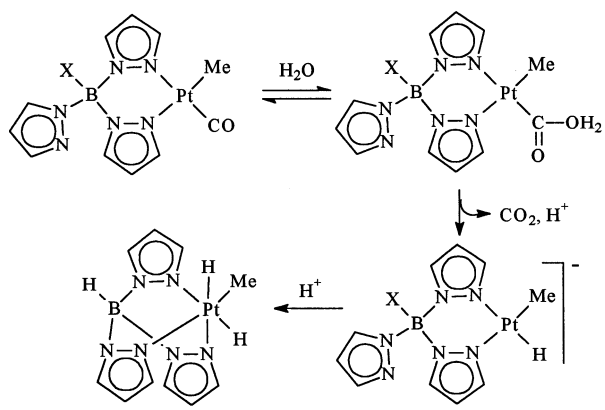
The reaction of $[PtMe_2(PN)]$, $PN = Ph_2PCH_2CH_2NMe_2$, with trimethoxysilane gives methane and $[PtMe\{Si(OMe)_3\}(PN)]$, and it is proposed that a short-lived hydridoplatinum(IV) intermediate $[PtHMe_2\{Si(OMe)_3\}(PN)]$ is formed by oxidative addition. The oxidative addition/reductive elimination sequence is assisted by the easy reversible dissociation of the Pt–N bond, and the corresponding complex $[PtMe_2(Ph_2PCH_2CH_2PPh_2)]$ fails to react with $HSi(OMe)_3$ [44]. A similar sequence may occur in the reaction of $[PtBu(SiYPh_2)L_2]$ with $HSiYPh_2$ to give $BuSiYPh_2$ and $[PtH(SiYPh_2)L_2]$, but with reductive elimination to form a Si–C bond [44].

6. Compounds formed by reaction of organoplatinum(II) complexes with water

A number of reactions of organoplatinum(II) complexes with water have been reported to give hydroxoplatinum(IV) complexes and, in some cases, the intermedi-

acy of hydridoplatinum(IV) complexes has been considered possible [34,45–47]. Hydrogen has been identified in some cases (though not quantitatively), as would be expected if a hydridoplatinum(IV) intermediate reacted with water to give a hydroxoplatinum(IV) product [34,45]. However, in some cases at least, it is now clear that oxygen is needed for the hydroxoplatinum(IV) complexes to be formed easily, so hydridoplatinum(IV) intermediates are not invoked as intermediates in these cases [35,48]. Methanol is a strong enough acid to give the protonation product of Eq. (18) reversibly [35].

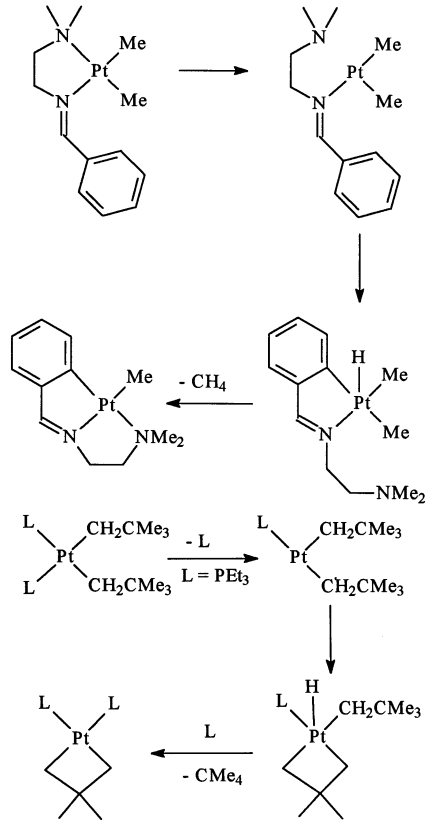
A certain example of hydride formation from water is shown in Eq. (27). The reaction of [PtMe(CO)Tp], Tp = $HBpz_3$, with water gave CO_2 and [PtH_2MeTp]. The reaction is suggested to occur by nucleophilic attack by water on the carbonyl ligand followed by loss of CO_2, and then protonation of the resulting hydrido(methyl)platinum(II) intermediate, as shown in simplified form in Eq. (27) [49]. It is now clear that some organoplatinum(II) complexes may be sufficiently electron-rich to be reversibly protonated by such weak acids as water and alcohols if protonation is accompanied by extra chelation [35,49].



(27)

7. Hydridoplatinum(IV) complexes formed by C–H bond activation

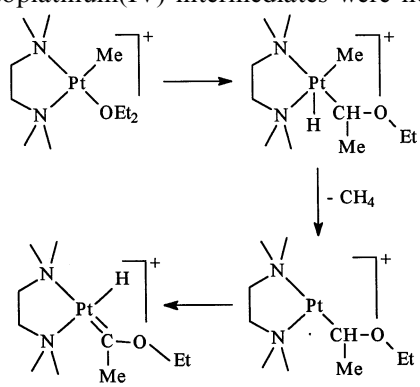
Hydridoplatinum(IV) intermediates have been proposed, but have not been detected directly, in orthometalation reactions using electron-rich organoplatinum(II) reagents, and a typical example is shown in Eq. (28) [50]. Similar intramolecular C–H bond activation is proposed in the formation of the platina(II)cyclobutane derivative [$Pt(CH_2CMe_2CH_2)(PEt_3)_2$] as shown in Eq. (28b) [51].



(28)

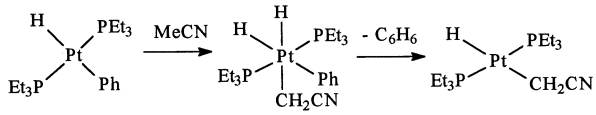
(28b)

Intramolecular metallation of weakly coordinated ether or tetrahydrofuran ligands has been established, leading to carbene complexes, as illustrated in Eq. (29) [52]. Again the hydridoplatinum(IV) intermediates were not directly detected.

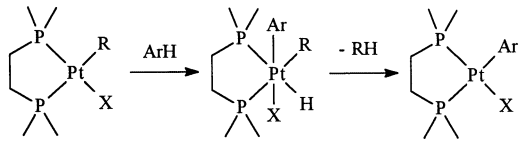


(29)

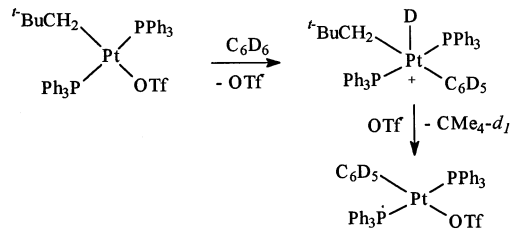
Intermolecular C–H activation is also proposed to give hydridoplatinum(IV) intermediates and selected examples are shown in Eqs. (30–32) [42,53,54]. In the reaction of Eq. (32) intermediate dissociation of triflate was proposed but ligand dissociation was not proposed in Eqs (30 and 31).



(30)

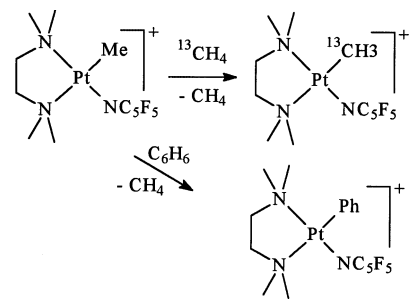


(31)

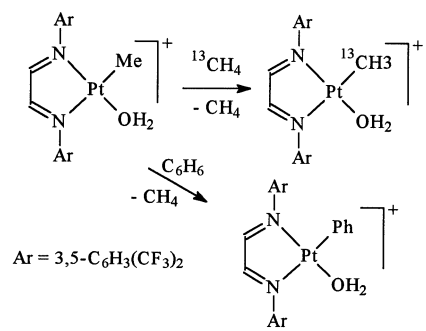


(32)

Intermolecular C–H activation of alkanes and arenes is accomplished using the weakly bound pentafluoropyridine complex $[PtMe(NC_5F_5)(tmeda)]^+$, as illustrated in Eq.(33). The reactions proceed by dissociation of pentafluoropyridine followed by C–H oxidative addition/reductive elimination and recoordination of pentafluoropyridine [52]. A similar mechanism is proposed using an aqua complex, as shown in Eq.(34). In this case, the reaction is carried out in a hydroxylic medium and easy dissociation of water is proposed prior to the C–H activation reactions [55].



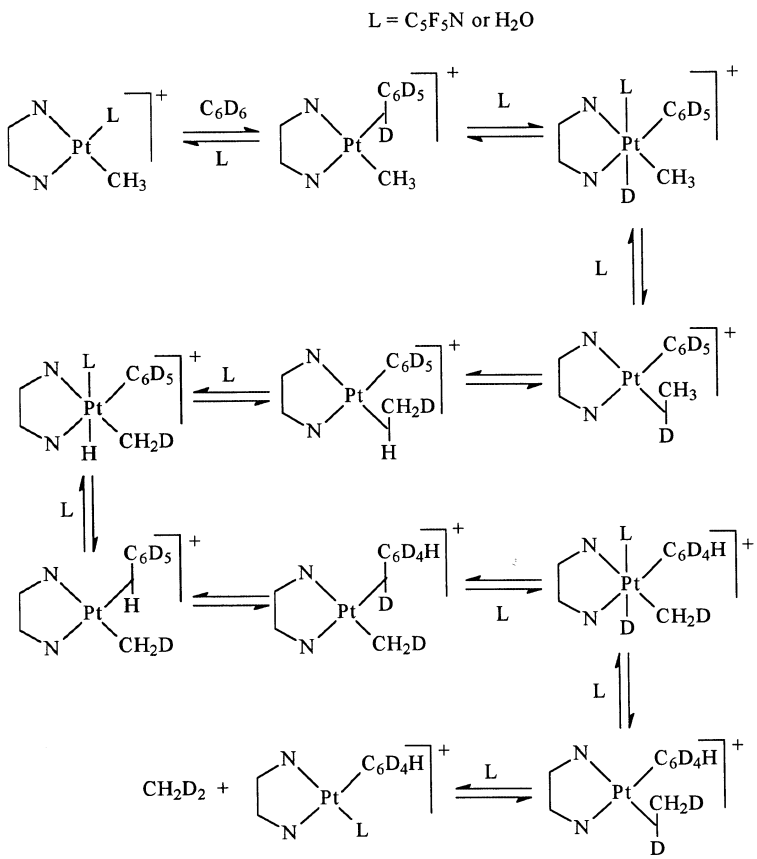
(33)



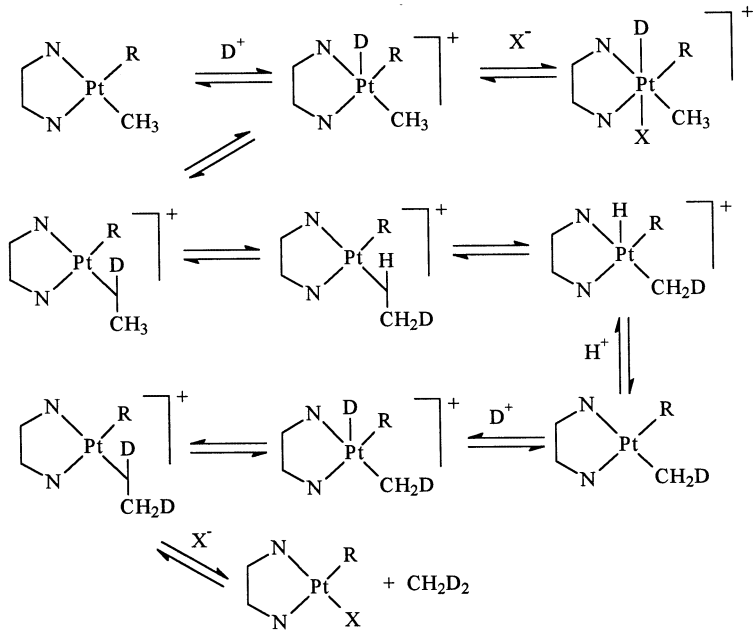
(34)

In some cases, the C–H reductive elimination step is reversible and this can lead to H–D exchange reactions [52,55]. The mechanism proposed for such exchanges is illustrated in Scheme 4, showing the sequence needed to form CH_2D_2. Repetition of the reactions shown in Scheme 4 can give multiply deuteriated methane mixtures.

Multiple H–D exchange can also be observed when alkanes are activated in acidic medium or when alkylplatinum(II) groups are cleaved by acid [2,3,30,32,36,37]. The reactions involved in this case are illustrated in Scheme 5 for formation of CH_2D_2. This may be observed in phosphine complexes as well as in the nitrogen-donor complexes illustrated in Scheme 5 [32]. Again the key step is reversibility of the C–H oxidative addition of coordinated methane, along with reversible protonation at platinum(II), which must be faster than the dissociation of methane from platinum(II). In unsymmetrical dimethylplatinum(II) complexes, the reaction may be selective. Thus, in $[PtMe_2(BPMA)]$, shown in Eq. (19). H–D exchange occurs selectively in the methylplatinum group *trans* to the amine and not in the methylplatinum group *trans* to pyridyl [36,37]. There is a correlation between



Scheme 4.

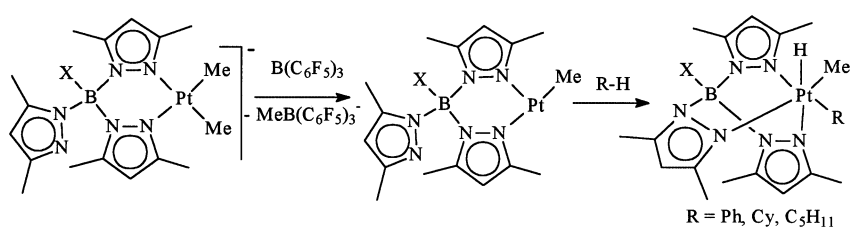


Scheme 5.

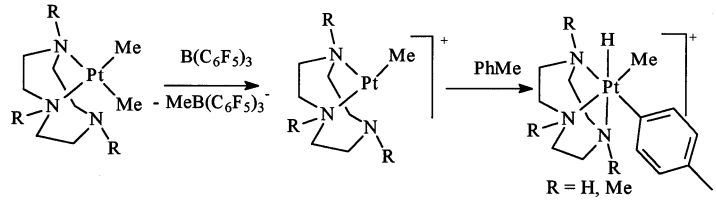
the presence and absence of H–D scrambling and the observation of a normal or inverse kinetic isotope effect [30,32].

In the methane activation step during catalytic oxidation of methane by sulfur trioxide in concentrated sulfuric acid, Scheme 6 ($X = HSO_4$), no conclusion was made on the possible intermediacy of platinum(IV) hydrides, but multiple deuterium incorporation into methane formed by reaction of preformed [PtClMe(bipym)] with D_2SO_4 was observed under comparable conditions [3].

In the above cases, the hydridoplatinum(IV) complexes are formed as short-lived reaction intermediates, but there are examples in which they may be formed as stable complexes. It is necessary that the products contain a strongly bound *fac*-tridentate ligand such as Tp′, and a 3-coordinate reactive platinum(II) substrate is formed by methyl anion abstraction using $B(C_6F_5)_3$ as shown in Eqs. (35 and 36) [56]. NMR data are included in Table 3.



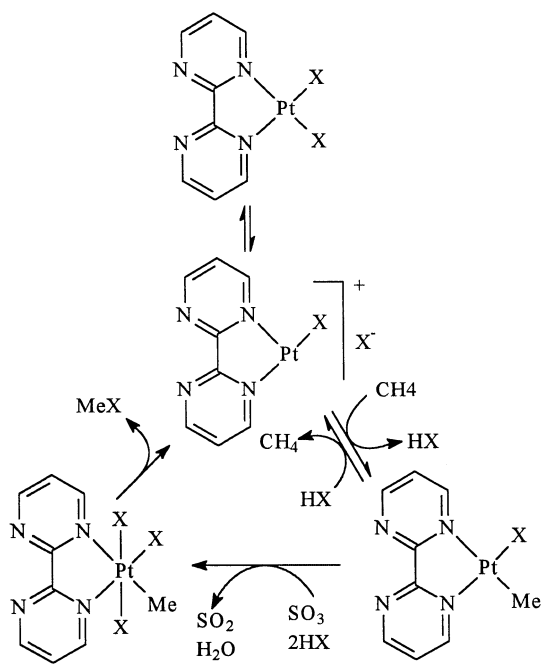
(35)



(36)

8. Reactions of hydridoplatinum(IV) complexes

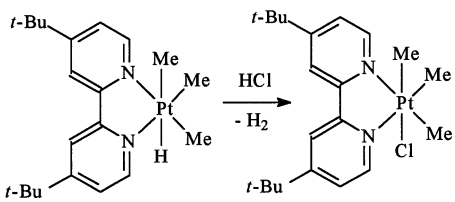
The most common reaction of the hydridoplatinum(IV) complexes is reductive elimination. Alkyl- and aryl(hydrido)platinum(IV) complexes that can easily undergo dissociation of a ligand to give a 5-coordinate intermediate decompose by C–H reductive elimination to give the corresponding alkane or arene and a platinum(II) complex. Several examples of such reactions have been described, as illustrated in Eqs. (8), (10), (19–22) and (29–32), and Schemes 4 and 5. Reductive elimination by H–H, H–Si, H–Ge, and H–Sn bond formation probably occurs in a similar way by concerted *cis* reductive elimination. If there is no ligand that can easily dissociate, the hydridoplatinum(IV) complexes appear stable to concerted *cis*-reductive elimination. The compounds can then be deprotonated by reaction with base and this also leads to the formation of platinum(II) complexes, as



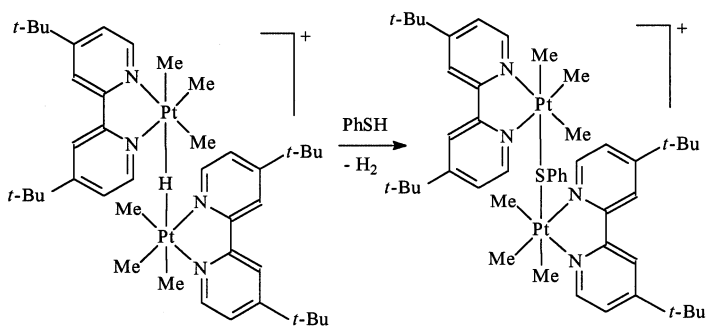
Scheme 6.

illustrated in Eqs. (17–19) and (21). A final form of reductive elimination involves the loss of H–X, probably by a two-step polar mechanism involving dissociation of X^- and deprotonation of the cationic hydridoplatinum(IV) intermediate so formed. Examples of these reactions are shown in Eqs. (1) and (3–6). An intramolecular deprotonation is illustrated in Scheme 3. These reductive elimination reactions are the reverse of those in which hydridoplatinum(IV) complexes are formed by oxidative addition, and the reactions can be easy and reversible. In most reductive eliminations involving hydridoplatinum(IV) complexes, the hydride ligand is eliminated but there is evidence that short-lived platinum(IV) intermediates containing PtHBu($SiPh_3$) or PtHMe($SiEt_3$) groups undergo selective C–Si reductive elimination to leave a hydridoplatinum(II) product [44,57].

A reaction that might be expected to occur easily is the substitution of the hydride ligand on platinum(IV) by using electrophilic reagents. For example, Pt(IV)–H with H–X might give H_2 and Pt(IV)–X, perhaps by way of a transient dihydrogen complex of platinum(IV). However, there are few well-defined examples of such reactions and several hydridoplatinum(IV) complexes are not easily decomposed in this way [30,31,35]. For example, triflic acid accelerates the decomposition of [PtHClR$_2$(TMEDA)] or [PtHR$_2$(Tp′)] by R–H reductive elimination when R = Me or CH_2Ph, perhaps by protonating nitrogen and so aiding formation of a 5-coordinate intermediate, but does not give H_2 as a product [30,33]. $[PtHMe_2(TACN)]^+$ is only slowly decomposed by triflic acid [35]. Early suggestions that the reaction of intermediates with Pt(IV)–H groups with water might give hydrogen and Pt(IV)–OH were undercut by the demonstration that oxygen was involved in the formation of the hydroxoplatinum(IV) products [45,46,48]. Only when the hydride is *trans* to a methyl group (or presumably other very strong σ-donors, though there appear to be no known examples) is it sufficiently hydridic in nature to react easily in this way [43]. Some examples in which hydridoplatinum(IV) complexes react as hydridic reagents are shown in Eqs. (25), (37) and (38).

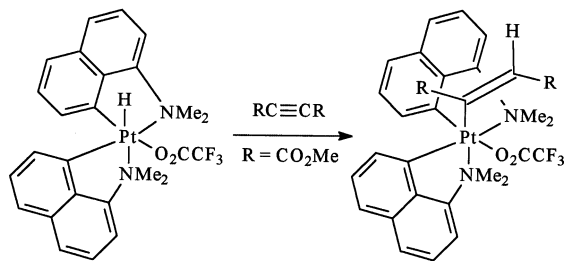


(37)



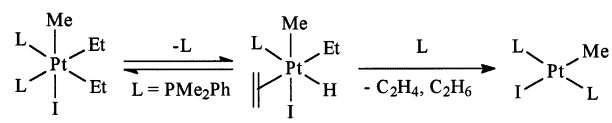
(38)

Hydridoplatinum(IV) complexes can undergo insertion reactions. Eq. (39) shows an acetylene with electron-withdrawing substituents inserts to give an alkenylplatinum(IV) complex with *Z* stereochemistry. The same product is formed from the NH···Pt(II) isomer. The stereochemistry is not consistent with a migratory insertion mechanism and either a polar or radical mechanism is proposed [28]. The corresponding bromide derivative **7** (Scheme 3) failed to react with the alkyne, and it is suggested that dissociation of the trifluoroacetate is a key intermediate step in the reaction of Eq. (39).

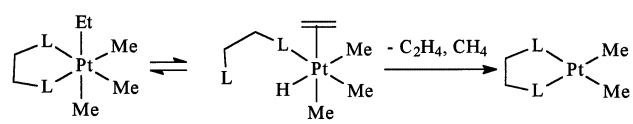


(39)

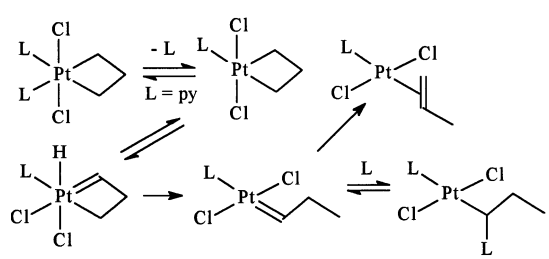
Simpler alkenes and alkynes failed to undergo insertion reactions with this hydride. The reverse β-elimination reaction is thought to be an important step in the thermolysis of ethylplatinum(IV) complexes as shown in Eqs. (40) and (40b). In this case, the hydridoplatinum(IV) intermediates were not directly detected. It is thought that ligand dissociation must occur to create a vacant site prior to the β-elimination step [58]. A similar mechanism has been proposed for the decomposition of platina(IV)cyclobutanes to give ylide or alkene complexes of platinum(II), but in this case α-elimination occurs as the primary reaction step leading to formation of the hydridoplatinum(IV) intermediate as shown in Eq. (40c) [58].



(40)

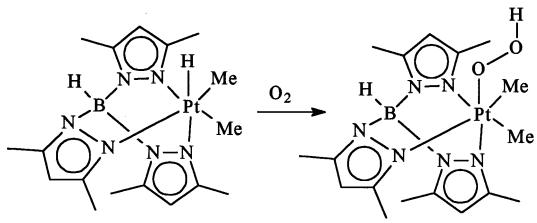


(40b)



(40c)

A particularly interesting insertion reaction occurs with dioxygen, to give a hydroperoxo complex, as shown in Eq. (41). This reaction is accelerated by light or by the radical initiator AIBN and so is proposed to occur by a radical chain mechanism [59]. Abstraction of the hydrogen atom from the hydridoplatinum(IV) complex gives a Pt(III) radical that combines with oxygen to give Pt–O–O•, and this then abstracts a hydrogen atom from the hydride to complete the cycle [59].



(41)

9. Theoretical studies of hydridoplatinum(IV) complexes

Several theoretical studies have been made of hydridoplatinum(IV) complexes, especially concerning their role in the activation of methane by platinum(II) complexes or in the protonolysis of methylplatinum(II) bonds.

In the activation of methane by *trans*-$[PtCl_2(OH_2)]$, the metathesis and oxidative addition mechanisms, in which the methane complex *trans*-$[PtCl_2(OH_2)(CH_4)]$ undergoes deprotonation or rearranges to $[PtCl_2(OH_2)H(CH_3)]$, respectively, as a key step, were considered to be competitive [60]. A study of the thermochemistry of the reaction of methane with model compounds related to the catalytic methane activation of Scheme 6 led to the conclusion that C–H oxidative addition to *cis*-$[Pt(NH_3)_2X(XH)]^+$, $X = HSO_4$, was highly endergonic and so unlikely to occur. However, the metathesis process leading to *cis*-$[Pt(NH_3)_2XMe]$ was found to be feasible [61]. These strongly electrophilic platinum(II) complexes behave rather like palladium(II) complexes, for which the palladium(IV) oxidation state is too strongly oxidizing to form easily from reagents like methane and so metathesis mechanisms are preferred [62]. In more electron-rich methylplatinum complexes, for example based on T-shaped $[Pt(en)Me]^+$, $en = H_2NCH_2CH_2NH_2$, coordination of methane to give a σ-complex $[Pt(en)Me(CH_4)]^+$ followed by oxidative addition to form $[Pt(en)HMe_2]^+$ was preferred over metathesis, and the oxidative addition product was stabilized compared to the σ-complex by ligand ($L = NF_2H$) coordination to make the octahedral hydridoplatinum(IV) complex [63]. The oxidative addition products are strongly stabilized by using *fac*-tridentate ligands, L_3, and the octahedral complexes *fac*-$[PtHMeClL_3]^+$ may then be strongly favored thermochemically over the reagents $[PtClL_3]^+$ and CH_4 [64].

Starting from 5-coordinate complexes *cis*-$[PtHMe_2L_2]^+$, $L = NH_3$ or PH_3, or $L_2 = en$, theory suggests a low activation energy for concerted reductive elimination to form the methane σ-complex *cis*-$[PtMe(CH_4)L_2]^+$, which is the resting state in all cases [63,65]. The reverse methane activation reaction was found to be easier with $L = NH_3$ than with $L = PH_3$, as seen in the energy level diagram of Fig. 1 [65].

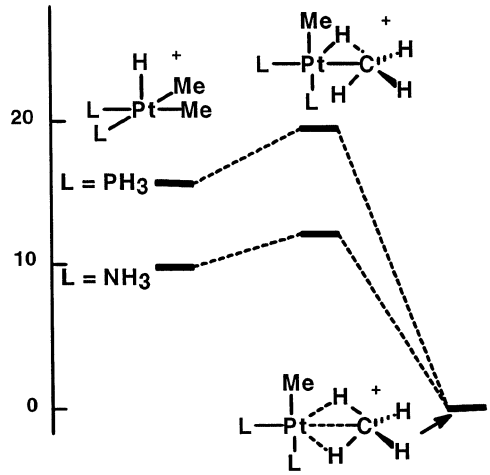


Fig. 1. The relative energies of two hydridoplatinum(IV) complexes and methane s-complexes and the transition states that connect them.

No easy route was found for reductive elimination of methane from the 6-coordinate all *cis* complex [$PtHMeCl_2L_2$], L = PH_3 [66], though such reactions are orbitally allowed and are known with several other octahedral d_6 complexes. Instead, dissociation of the ligand *trans* to hydride occurred as the transition state to C–H reductive elimination was approached. In contrast, C–H reductive elimination from the platinum(II) complex [$PtHMeL_2$] occurred without ligand dissociation [66,67]. In both cases, reductive elimination is easier for the coordinatively unsaturated complex, but ligand dissociation requires less energy in the platinum(IV) case. This provides the basis for the difference in mechanisms in the two cases [66].

Most of the recent theoretical studies have used density functional theory (DFT) as the method of choice since it is able to treat complex molecules, containing the heavy atom platinum and so requiring relativistic corrections to be applied, with the best available combination of accuracy and computing efficiency.

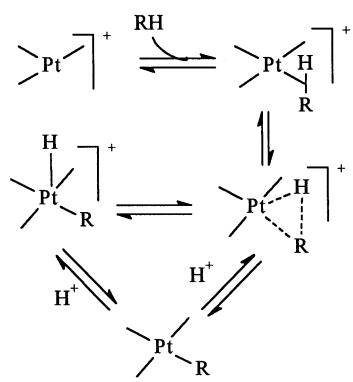
10. Conclusions

Hydridoplatinum(IV) complexes are now firmly established both as stable compounds and as short-lived reaction intermediates. In most cases so far reported, it seems that the easy formation or decomposition of hydridoplatinum(IV) complexes requires coordinatively unsaturated intermediates. This is explicit in the formation of hydridoplatinum(IV) complexes by protonation of 16-electron square-planar platinum(II) precursors or by concerted oxidative addition of C–H bonds of alkanes or arenes to 14-electron T-shaped platinum(II) precursors, and also in the proposed formation by α- or β-elimination reactions. It is less obvious in the formation of hydridoplatinum(IV) complexes from metal hydrides and platinum-

(IV) precursors, as for example in Eqs. (25-26), but it should be noted that ligand substitution in octahedral platinum(IV) complexes usually occurs by a dissociative mechanism in organometallic derivatives so the correlation remains good. Similarly, decomposition of hydridoplatinum(IV) complexes by reductive elimination also occurs after ligand dissociation, and the 5-coordinate intermediates usually have square pyramidal structures (the alternative being a distorted "pinched" trigonal pyramidal structure [65]). The theoretical and experimental studies are self-consistent in this regard.

There are likely to be exceptions to the above rules. If ligand dissociation is sufficiently difficult then C–H reductive elimination from octahedral complexes may be expected. Similarly, E–H oxidative addition might occur at square-planar platinum(II) complexes if the ligand dissociation is difficult and the E–H bond sufficiently reactive. It is possible that some of the oxidative additions involving Si–H, Ge–H or Sn–H bonds might occur in this way (Eq. (24) for example). The extent of free radical chemistry in the formation and reactivity of hydridoplatinum(IV) complexes is largely unexplored, and could be extensive also [59].

In terms of the role of hydridoplatinum(IV) intermediates in protonolysis of alkyl- or aryl- platinum(II) bonds and in the activation of alkanes or arenes by platinum(II), they are now very well established in many cases by recent research. However, they are not necessarily formed in all cases and the alternative metathesis mechanism for C–H bond activation might be important for the most electron-deficient platinum(II) reagents, for which oxidation to platinum(IV) is particularly unfavorable [53,61]. This is likely also the case in the protonolysis reactions, which usually occur by oxidative addition/reductive elimination but which may also occur by the classical S_E2 mechanism if proton addition at platinum is disfavored for either steric or electronic reasons (Eqs (10 and 11) for example). The situation is summarized in simplified form in Scheme 7. It should be noted that coordinatively unsaturated T-shaped platinum(II) or square pyramidal platinum(IV) complexes will be formed transiently from square planar or octahedral complexes respectively and that proton addition/loss will always be mediated intramolecularly or intermolecularly by solvent molecules, anions or added bases.



Scheme 7.

Note added in proof

The following significant papers have been published recently. H. Heiberg, L. Johansson, O. Gropen, O.B. Ryan, O. Swang and M. Tilset, 'A combined experimental and density functional theory investigation of hydrocarbons activation at a cationic platinum(II) diimine aqua complex under mild conditions', J. Am. Chem. Soc. 122 (2000) 10831. L. Johansson, M. Tilset, J.A. Labinger and J.E. Bercaw, 'Mechanistic investigation of benzene C–H activation at a cationic platinum(II) center: Direct observation of a platinum(II) benzene adduct', J. Am. Chem. Soc. 122 (2000) 10846. L. Johansson and M. Tilset, 'Evidence for associative methane loss following protonation of (diimine)$Pt(CH_3)_2$: Three-coordinate 14-electron cations $L_2PtCH_3^+$ are not necessarily intermediates in C–H activation at cationic Pt complexes', J. Am. Chem. Soc. 123 (2001) 739. T.M. Gilbert, I. Hristov and T. Ziegler, 'Comparison between oxidative addition and σ-bond metathesis as possible mechanisms for the Catalytica methane activation process by platinum(II) complexes: A density functional theory study', Organometallics (2001) in press.

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