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Bridging and Terminal (Phosphanido)platinum Complexes

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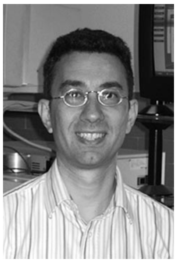
The PR_2^- group (the phosphanido group, according to the modern IUPAC rules) possesses a strong nucleophilicity, a high bridging tendency and a remarkable flexibility. This review addresses the issue of (phosphanido)platinum complexes, subdividing them into terminal and bridging species. Terminal (phosphanido)platinum complexes are usually prepared by deprotonation of a coordinated secondary (or primary) phosphane on a cationic Pt^{II} complex, by an appropriate base. The terminally bonded phosphanide group shows no tendency to form multiple bonds with platinum: in all crystallographically characterised Pt complexes, the terminal phosphanido P atom is pyramidal. Due to the high nucleophilicity granted by the presence of the active lone pair on P, terminal (phosphanido)platinum complexes react with molecules such as O_2 and S_8, and they can be used for the synthesis of dimetallic compounds upon reaction with suitable metal fragments. The known Pt^I phosphanido-bridged complexes are dinuclear, diamagnetic and endowed with a strong Pt–Pt bond. The μ-PPh_2 bridge in Pt^I dimers arises often by (thermal) activation of the P–C bond in coordinated PPh_3 or dppm. Pt^I phosphanido-bridged complexes are also prepared by reaction of (dichlorido)platinum complexes with reagents such as Na, NaOH, alcohols. For such complexes a multifaceted reactivity, including the substitution of a terminal ligand, the reaction with electrophiles such as H^+ and its isolobal analogues, the insertion into the μ-P–Pt bond, has been reported. Hydridophosphanido complexes are formed by oxidative addition of a P–H bond onto zero-valent Pt complexes, by protonation of Pt^I dimers or by action of BH_4^- on halido species. Dehydrochlorination of secondary (and primary) phosphane complexes gives chlorido complexes which are mostly prepared in the *anti*-$[(PRR'_2)(Cl)Pt(\mu\text{-}PR''_2)]_2$ geometry. Chiral complexes are obtained when asymmetric phosphanido P atoms are present in the molecule. A rich coordination chemistry has been developed on organometallic phosphanido Pt complexes bearing the pentafluorophenyl group. In this framework, a great number of Pt complexes of various nuclearity have been crystallographically characterised and their reactivity towards oxidants studied. The class of polynuclear phosphanido Pt complexes is represented by triangulo species, in which the bridging phosphanide group is typically μ-PPh_2 or μ-P*t*Bu_2, by linear complexes of various nuclearity and by bent species stemming from the presence of a triply bridging diphenylphosphanido ligand in the molecule. Applications of phosphanido Pt complexes in catalysis and materials chemistry are also discussed.

1. Introduction

The chemistry of diorganophosphanido (PR_2^-) complexes has been the object of extensive studies and still attracts great attention[1] on account of the ability of such ligands to support both strongly bonding and non-interacting metal centres.

Phosphanido-bridged complexes of transition metals have a history of almost 50 years: the first member of this series, reported in 1960, is the dimeric palladium(II) complex $[Pd(Cl)(\mu\text{-}PPh_2)(PPh_2H)]_2$,[2] which was at that time not recognised as a phosphanido-bridged complex.[3] In the following years, a lively research led to the synthesis and characterisation of hundreds of new polynuclear compounds characterised by one or more phosphanido groups bridging two (or more) metal atoms. While historically phosphanido bridges were used as flexible ligands able to endow clusters and dimetallic complexes with reduced (un-



Piero Mastrorilli was born in 1966 and educated in Bari, Italy. He studied chemistry at the Faculty of Science (1984–1989), where he also received his Ph.D. in 1993 in inorganic chemistry and catalysis, under the supervision of Professor Adriano Sacco. He spent one year in the Technical University of Aachen under the supervision of Professor Wilhelm Keim. He is now a professor at the Polytechnic of Bari. His research interests include coordination chemistry, catalysis and π-conjugated materials.

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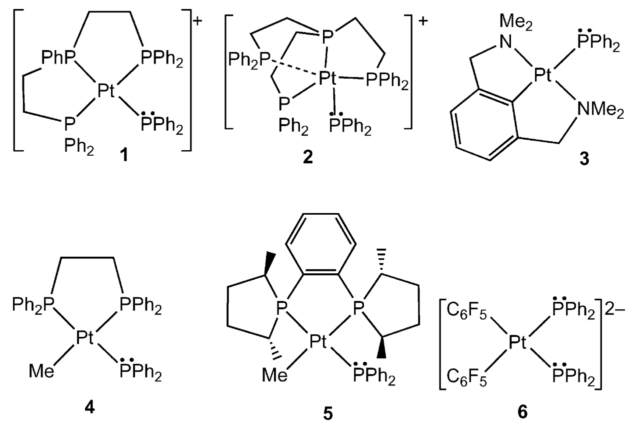
desirable) fragmentation, it is now assumed that coordinated phosphanides can exhibit a multifaceted reactivity.[4] Two recent examples drawn from platinum chemistry are the reversible transformation of two diphenylphosphanido ligands into the neutral tetraphenyldiphosphane ligand[5] and the reversible coupling of alkynyl and di-*tert*-butylphosphanido ligands.[6] A wide variety of coordination modes is known for phosphanido groups in Pt complexes. Examples exist with a Pt–PR_2 bound to a main group element (Li,[7] B[8]) or to the electrophilic fragment $[M'PPh_3]^+$ (M′ = Ag, Au).[9,10] Moreover, there are several complexes in which phosphanido groups act as terminal or triply bridging (μ_3) ligands, and polymeric $[Pt(PPh_2)]_n$ species[11] have also been reported. However, the majority of phosphanido Pt complexes contains PR_2 groups bound in a μ_2 coordination mode. The presence of a Pt–Pt bond in μ_2-PR_2 Pt dimers is indicated by ^{31}P NMR spectroscopy: low-field signals for μ_2-PR_2 groups (100–400 ppm) are indicative of the presence of a Pt–Pt bond.[12] Predictions on the presence of Pt–Pt bonds can also be made on the basis of electron counting rules. Given that Pt obeys the "16 e rule"[13] and that, according to the effective atomic number (EAN) rules,[14] the bridging phosphanido group acts formally as a 3 e donor (covalent model), the number of Pt–Pt bonds in polynuclear phosphanido-bridged complexes can be calculated as: $[(16 \times n_{Pt}) - VEC]/2$, where n_{Pt} is the number of Pt atoms in the complex (or cluster) and VEC is the valence electron count. Alternatively, for dinuclear Pt compounds, a framework electron count of 4 or 6 can be taken as indicative of the presence of a Pt–Pt bond.[15]

Recently, a review on the chemistry of dinuclear Pd^{II} and Pt^{II} complexes appeared, which succinctly gives an idea of the potentialities of the bridging phosphanides in palladium and platinum dimers.[16]

The aim of this microreview is to supply the reader with a survey of the known platinum complexes bearing a PR_2 or PHR group coordinated either in a bridging or in a terminal mode and to trace the developments that this chemistry may have in the future. The treatment starts with terminal phosphanido complexes, continues with phosphanido-bridged dinuclear complexes (subdivided into Pt^I compounds, hydrido complexes, halido and aryl or alkyl complexes), and ends with polynuclear homometallic compounds. A paragraph is also devoted to applications of these compounds in catalysis and materials chemistry.

2. Terminal (Phosphanido)platinum Complexes

Although in the first paper on phosphanido-bridged complexes of platinum it was suggested that "it seems unlikely that terminal diphenylphosphido groups can exist in the platinum(II) series except under very special circumstances",[17] the following stable Pt^{II}–PPh_2 complexes are currently known: $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2)]^+$, (**1**)[18] $[Pt\{P(CH_2CH_2PPh_2)_3\}(PPh_2)]^+$ (**2**),[18] $[Pt(NCN)(PPh_2)]$ (NCN = $C_6H_3\{CH_2NMe_2\}_2$) (**3**)[19] $[Pt(dppe)(Me)(PPh_2)]$ (**4**)[20] and $[Pt\{(R,R)\text{-Me-Duphos}\}(Me)(PPh_2)]$, (**5**)[21] the latter having been characterised also by XRD (Scheme 1). Moreover, complex $[Pt(C_6F_5)_2(PPh_2)_2]^{2-}$ (**6**), containing *two* terminal diphenylphosphanido ligands can be prepared in situ.[22] Other non-isolable terminal phosphanido Pt complexes are *trans*-$[Pt(PEt_3)_2(X)(PX'_2)]$ (X and X′ are halides, **7**),[23] *cis*-$[Pt(PEt_3)_2(Cl)\{P(SiMe_3)R\}]$ (R = $SiMe_3$, **8a**; R = *t*Bu, **8b**), *trans*-$[Pt(PEt_3)_2(Cl)\{P(SiMe_3)_2\}]$ (**8c**) and *trans*-$[Pt(PEt_3)_2\{P(SiMe_3)_2\}_2]$ (**8d**).[24]



Scheme 1. Terminal diphenylphosphanido Pt^{II} complexes.

The most frequently exploited procedure for preparing a terminal phosphanido complex is the deprotonation of a coordinated secondary (or primary) phosphane by an appropriate base, which in some instances may be previously coordinated onto the metal atom. Most of the terminal phosphanido Pt complexes used by Glueck and co-workers in their studies on fundamental chemistry and catalytic activation of P–H bonds were prepared by this procedure.[25] Such complexes have the general formula [(P^P)Pt(X)(PRR′)], in which P^P = chelating diphosphane, X = H, Me, $C(O)C_3F_7$, CH(Me)CN, CH_2CH_2CN, and R, R′ = H, alkyl or aryl groups.[21,26]

Deprotonation of $[PtCl(PHCy_2)_3]^+$ affords the dicyclohexylphosphanido complex *trans*-$[PtCl(PHCy_2)_2(PCy_2)]$ (**9**), whose XRD structure is shown in Figure 1.[27] Dynamic NMR spectroscopic studies revealed that **9** exhibits a dynamic process with an activation free energy ($\Delta G^{\ddagger}$) value of 34 kJ/mol.[28] In light of the bulkiness of the ligands surrounding the Pt atom and the known relatively rapid inversion in phosphanido complexes of metals, the dynamic pro-

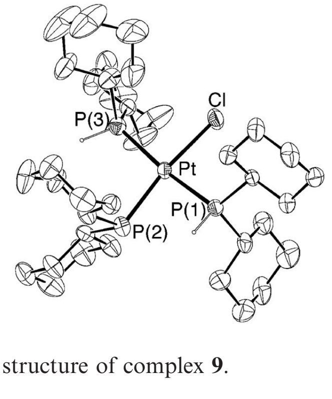
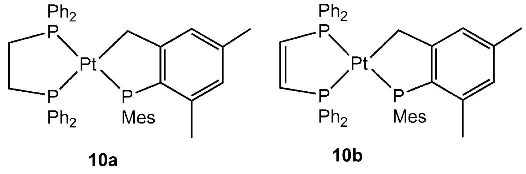


Figure 1. X-ray structure of complex **9**.

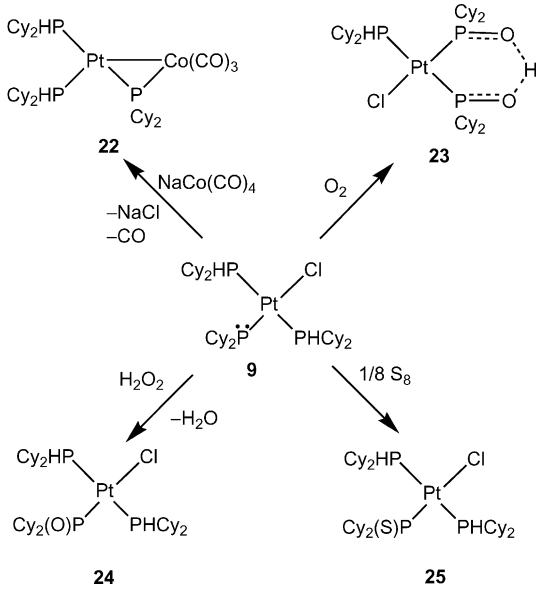
cess found for **9** can be assigned either to a slow P inversion in the pyramidal phosphanide group or to a hindered rotation about the P^2–Pt bond (or to a combination of them). However, comparison with the $\Delta G^{\ddagger}$ values found by Glueck for cyclometalated dimesityl phosphanide complexes **10a**,**b** (for which pure inversion barriers of 56 kJ/mol have been calculated, Scheme 2)[29] shows that hindered rotation is favoured as the dynamic process for **9**. This hypothesis is substantiated by the marked pyramidal geometry found for P^2 in the X-ray crystal structure,[30] which increases the energy difference between the planar transition state for the inversion and the pyramidal ground state.



Scheme 2. Cyclometalated dimesitylphosphanido Pt complexes.

A distinctive NMR spectroscopic feature of terminal phosphanido Pt compounds is the low value (< 1500 Hz, often below 1000 Hz) of the direct $^1J_{P-Pt}$ constant of the terminal phosphanido P atom (Table 1) as a consequence of the low s character of the P–Pt bond. The terminally bonded phosphanide group shows no tendency to form multiple bonds with platinum: in all crystallographically characterised Pt complexes the terminal phosphanido P is pyramidal, and the sum of the angles at P ranges from 306.2 to 333.9° (Table 1). The P–Pt distances range from 2.326(3) Å to 2.4117(10) Å.

The lone pair on the phosphorus atom in terminal phosphanido complexes renders such molecules highly reactive and capable of acting as ligands to other metals: reaction of **3** with $[Pt(NCN)H_2O]^+$ yielded the dimetallic compound $[\{Pt(NCN)\}_2(\mu\text{-}PPh_2)]^+$,[19] while reaction of **4** with [(dppe)-Pt(Me)(OTf)] gave $[\{Pt(dppe)(Me)\}_2(\mu\text{-}PPh_2)]^+$,[31] reaction of **6** with $[Pt(dppm)Cl_2]$ gave $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2\text{-}Pt(dppm)]$,[22] however, and reaction of **9** with $Na[Co(CO)_4]$ gives the dicyclohexylphosphanido-bridged species **22** (Scheme 3).[32]



Scheme 3. Reactivity of complex **9**.

Complex **9** reacts promptly also with molecules like H_2O_2, O_2 and S_8, giving the products shown in Scheme 3. The reactivity of **9** is peculiar in the panorama of terminal phosphanido complexes, as the molecule contains reactive P–H bonds. Thus, while reaction with O_2 usually transforms the $M–PR_2$ fragment into $M–P(O)R_2$, reaction of **9** with O_2 gives selectively the hydrogen-bonded bis(phosphinito) complex $[PtCl(PHCy_2)\{(PCy_2O)_2H\}]$ (**23**).[33] The Pt–$P(O)Cy_2$ species *trans*-$[Pt(Cl)(PHCy_2)_2\{P(O)Cy_2\}]$ (**24**) can be obtained by action of hydrogen peroxide (Scheme 3). The uptake of 1 equiv. S transforms **9** into the κP-dicyclohexylthiophosphinito complex *trans*-$[Pt(Cl)(PHCy_2)_2\{P(S)\text{-}$

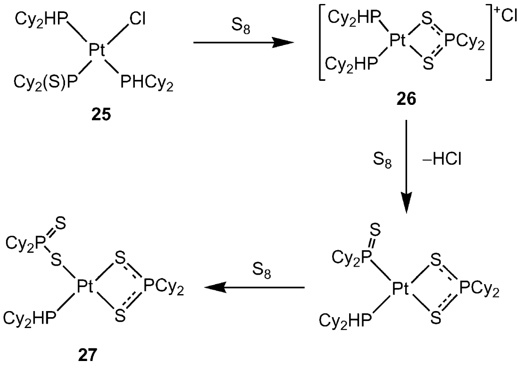
Table 1. P–Pt interatomic distances and ^{31}P NMR spectroscopic parameters (at room temperature) for selected terminal phosphanido Pt^{II} complexes.[a]

Complex	d_{Pt-Pt} [Å]	ΣP angles [°]	δ_{PR_2} [ppm]	$^1J_{Pt-PR_2}$ [Hz]	Ref.
[Pt(dppe)(Me)(PHMes*)] (**11**)	2.378(5)	–	–71.1	863	[26c]
$[Pt(dppe)(Me)(PMes_2)]$ (**12**)	2.351(2)	333.9	–56.4	1239	[26c]
[Pt(*S*,*S*-Chiraphos)(Me)(PPhIs)] (**13**)	2.3622(15)	333.3	–21.0	1126	[26e]
$[Pt(dcpe)(CH_2CH_2CN)(PHMes^*)]$ (**14**)	2.390(2)	–	–83.7	806	[26f]
[Pt(Me-Duphos)(H)(PPhIs)] (**15**)	2.335(5)	326.6	–28.0	1153	[26g]
trans-$[Pt(PHCy_2)_2(Cl)(PCy_2)]$ (**9**)	2.326(3)	320.5	20.6	931	[34]
[Pt(*R*,*R*-Me-Duphos)(Me){PPh(*i*Bu)}] (**16**)	2.372(4)	306.2	–57.3 and –63.9[b]	999 1011	[26h]
[Pt(*R*,*R*-Me-Duphos)(Ph)(PMeIs)] (**17**)	2.3761(13)	320.6	–51.8	899	[26i]
[Pt(*R*,*R*-*i*Pr-Duphos)(Ph)(PMeIs)] (**18**)	2.370(2)	323.3	–60.0	[c]	[26i]
[Pt(*R*,*R*-Me-Duphos)(I)(PMeIs)] (**19**)	2.3996(19)	321.3	–68.3	842	[26i]
[Pt(*R*,*R*-Me-Duphos)(Cl)(PMeIs)] (**20**)	2.3926(16)	316.5	–55.0 and –36.0[b]	809 [c]	[26i]
$[Pt(R,R\text{-Me-Duphos})(PMeIs)_2]$ (**21**)	2.4117(10)	321.4	–56.7	[c]	[26i]
$[Pt(R,R\text{-Me-Duphos})(Me)(PPh_2)]$ (**5**)	2.3822(18)	318.4	–28.9	1077	[21]

[a] Abbreviations: Mes* = 2,4,6-$(tBu)_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$; Is = 2,4,6-$(iPr)_3C_6H_2$; *S*,*S*-Chiraphos = (2*S*,3*S*)-bis(diphenylphosphanyl)butane; Me-Duphos = 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene; *i*Pr-Duphos = 1,2-bis[(2*R*,5*R*)-2,5-diisopropylphospholano]benzene. [b] For the two diastereoisomers. [c] Not given because of signal broadness.

Cy_2}] (**25**). Both **24** and **25** show hindered rotation about the P(E)–Pt bond (E = O, S) with $\Delta G^{\ddagger}$ values of 46 and 37 kJ/mol, respectively.[28]

The reactivity of the ancillary $PHCy_2$ ligands in **9** is shown in the sulfuration carried out with excess S_8 leading eventually to [Pt(κ^2*S*,*S*′-PCy_2S_2)(κ*S*-PCy_2S_2)($PHCy_2$)] (**27**, Scheme 4). Monitoring of the reaction showed that it proceeds stepwise, the first two S atoms attacking the terminal phosphanido P and further two S atoms attacking one of the bound $PHCy_2$ ligands.[27]



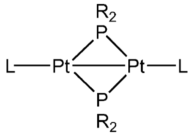
Scheme 4. Stepwise sulfuration of complex **25**.

The presence of P–H moieties in ionic compounds {such as [Pt(κ^2*S*,*S*′-PS_2Cy_2)($PHCy_2$)$_2$]Cl, **26**} is responsible also for hydrogen-bonding-type interactions with chloride counteranions, which were studied by NMR spectroscopic methods. Two features that can be taken as a hint for P–H···Cl interactions are: (i) the remarkable change in the chemical shift for the P and H atoms involved in the hydrogen-bonding interaction when the $^{31}P\{^1H\}$ and ^1H NMR spectra are recorded in solvents with different polarity (typically C_6D_6 and CD_3CN); (ii) the absence of the ^{35}Cl NMR signal in halogenated solvents *and* the appearance of a ^{35}Cl NMR signal after addition of a few drops of methanol.[28]

3. Phosphanido-Bridged Dinuclear Platinum Complexes

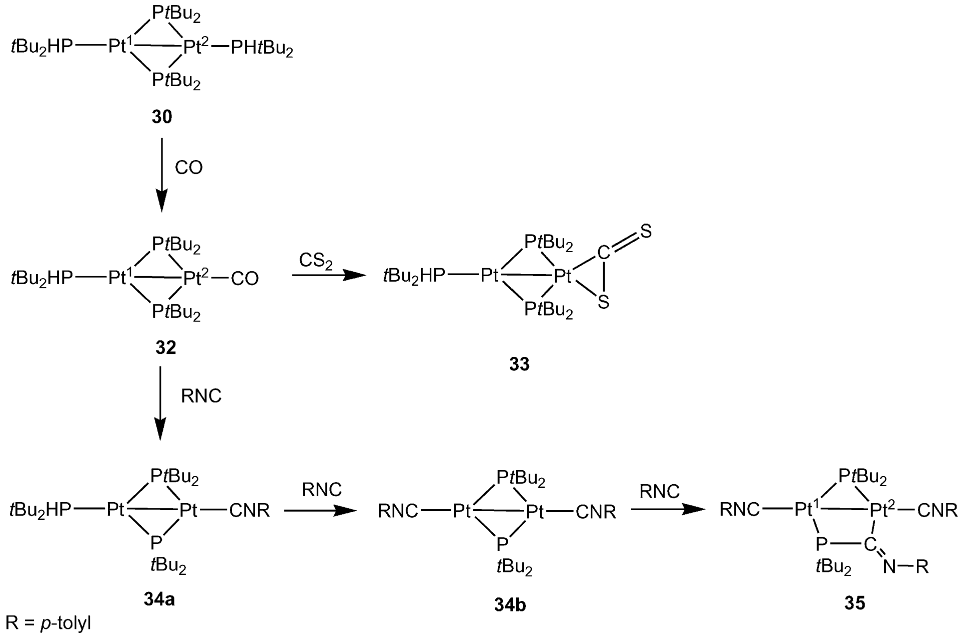
3.1. Pt^I Compounds

All known phosphanido-bridged Pt^I complexes are dinuclear, diamagnetic and endowed with a strong Pt–Pt bond. The nature of this bond in structurally characterised Pt^I (and Pd^I) dimers has been investigated from a theoretical point of view.[35] The first described Pt^I phosphanido species was complex [(PPh_3)Pt(μ-PPh_2)]$_2$*(Pt–Pt)* (**28**, Scheme 5), which is one of the thermolysis products of [Pt(PPh_3)$_4$].[36] The same structure, featuring two terminal P ligands *trans* to the Pt–Pt bond, was found in dimers **29**–**31**. Complex [(PEt_3)Pt{μ-P($SiMe_3$)$_2$}]$_2$*(Pt–Pt)* (**29**) was obtained by reaction of [$PtCl_2$(PEt_3)$_2$] with LiP($SiMe_3$)$_2$.[24] [(PH*t*Bu_2)Pt(μ-P*t*Bu_2)]$_2$*(Pt–Pt)* (**30**), which is one of the products of Na reduction of *trans*-[$PtCl_2$(PH*t*Bu_2)$_2$],[37] can be prepared by deprotonation of the corresponding terminal hydride species with *n*-butyllithium.[7] Carbonylation of **30** gives [(PH*t*Bu_2)Pt(μ-P*t*Bu_2)$_2$Pt(CO)]*(Pt–Pt)* (**32**), which, in turn, reacts (i) with CS_2 to give the product of CO substitution [(PH*t*Bu_2)Pt(μ-P*t*Bu_2)$_2$Pt(CS_2)]*(Pt–Pt)* (**33**),[7]



28 R = Ph, L = PPh_3
29 R = $SiMe_3$, L = PEt_3
30 R = *t*Bu, L = PH*t*Bu_2
31 R = Cy, L = $PHCy_2$

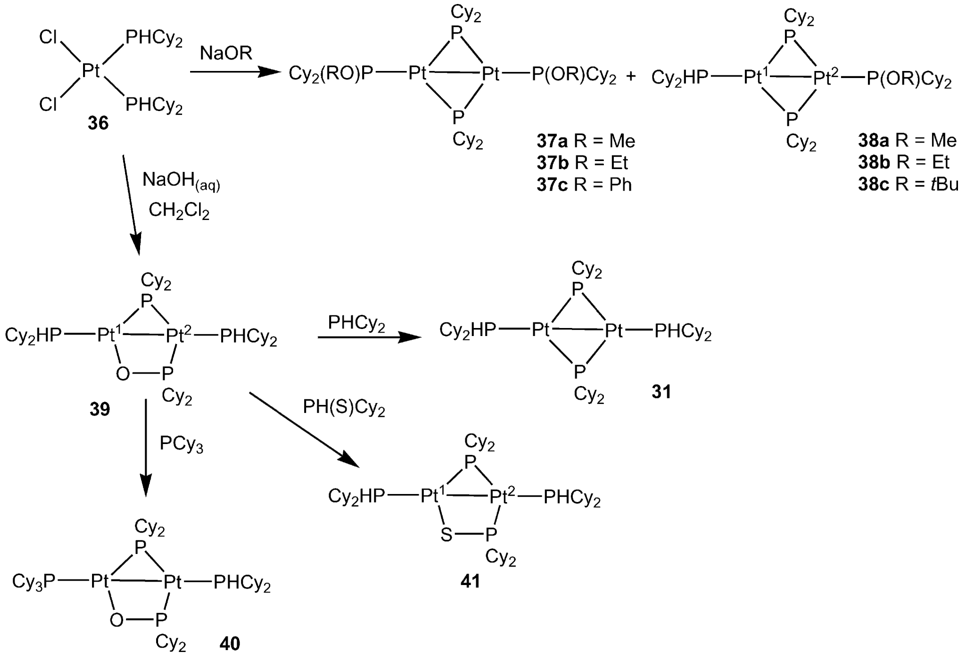
Scheme 5.



Scheme 6. Di-*tert*-butylphosphanido Pt^I complexes.

(ii) with *p*-tolylisonitrile to give [(L)Pt(μ-P*t*Bu$_2$)$_2$Pt(CNR)]*(Pt–Pt)* (**34a**,**b**) and, with 3.5 equiv. isocyanide, the product of isocyanide insertion into the Pt–P bond of the phosphanido bridge, [Pt$_2$(μ-P*t*Bu$_2$){μ,η^2-P(*t*Bu$_2$)C(=N-*p*-tolyl)}(CN-*p*-tolyl)$_2$]*(Pt–Pt)* (**35**, Scheme 6).[38] Complex [(PHCy$_2$)-Pt(μ-PCy$_2$)]$_2$*(Pt–Pt)* (**31**) forms by sodium reduction of *cis*-[Pt(PHCy$_2$)Cl$_2$] (**36**) at room temperature.[34] Symmetrical and unsymmetrical terminal diorganophosphinito Pt^{I} complexes (complexes **37** and **38**, respectively) are obtained by reaction of **36** with sodium alkoxides or phenoxide (Scheme 7).[39] For [{P(OMe)Cy$_2$}Pt(μ-PCy$_2$)]$_2$*(Pt–Pt)* (**37a**), the XRD structure shows a planar Pt$_2$P$_2$ core (Figure 2). When a dichloromethane solution of **36** is reacted with NaOH$_{(aq.)}$ the mixed bridged system [(Cy$_2$PH)Pt(μ-PCy$_2$)(κ^2*P,O*-μ-Cy$_2$PO)Pt(Cy$_2$PH)]*(Pt–Pt)* (**39**) forms, featuring a bridging dicyclohexylphosphinito ligand (Scheme 7 and Figure 2).[39] Dialkylphosphinito-bridged homodinuclear complexes are interesting (albeit rare) compounds, as the differentiation of the two metal centres brought about by the combination of a soft donor (P) and a hard ligand (O) may result in peculiar reactivity. Thus, complex **39** behaves as an amphiphilic molecule, that is, it reacts both with electrophiles and with nucleophiles. The reactivity of **39** with electrophiles (namely Brønsted acids) will be illustrated in the section dedicated to hydrido compounds, whereas the reactivity towards P nucleophiles such as PHCy$_2$, PCy$_3$ and PH(S)Cy$_2$, leading to **31**, [(Cy$_3$P)Pt(μ-PCy$_2$)(κ^2*P,O*-μ-Cy$_2$PO)Pt(Cy$_2$PH)]*(Pt–Pt)* (**40**) and [(Cy$_2$PH)-Pt(μ-PCy$_2$)(κ^2*P,S*-μ-Cy$_2$PS)Pt(Cy$_2$PH)]*(Pt–Pt)* (**41**), respectively, is outlined in Scheme 7.[40] Mechanistic studies carried out on these reactions showed that in all cases the incoming nucleophile attacks the oxygen-bound Pt atom, which represents the most electrophilic site of the molecule, as confirmed by DFT studies. The role played by the bridging phosphanide is that of maintaining the integrity of the dinuclear metal core throughout the various steps of the reactions.

The mixed-bridge Pt^{I} systems [Pt$_2$(μ-PPh$_2$)(μ-dppm)-(PPh$_3$)$_2$]$^+$*(Pt–Pt)* (**42**)[41] and [Pt$_2$(μ-PPh$_2$)(μ-dppm)(nor-



Scheme 7. Dicyclohexylphosphanido Pt^{I} complexes.

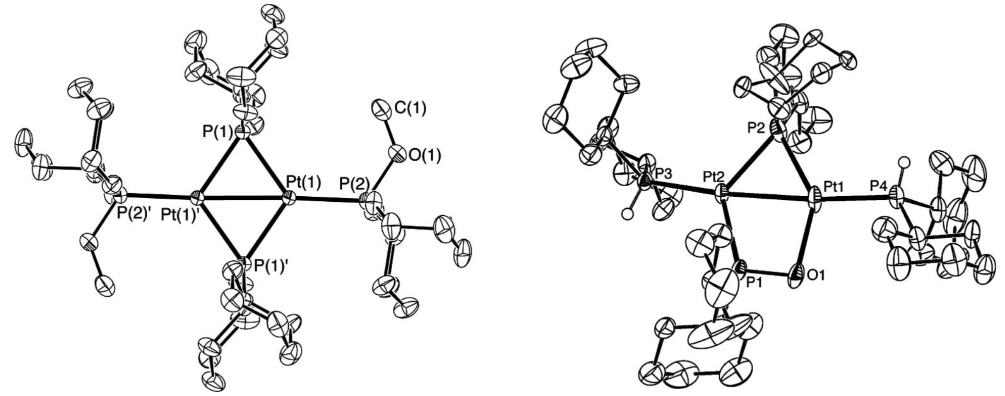
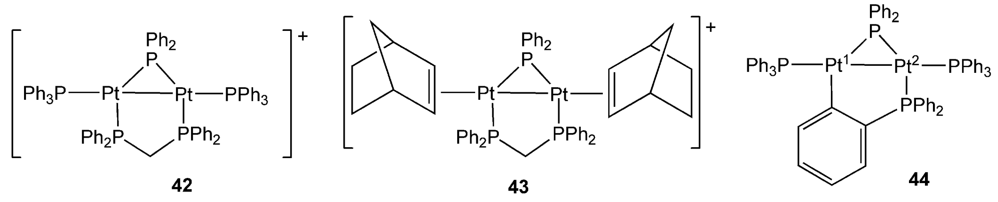
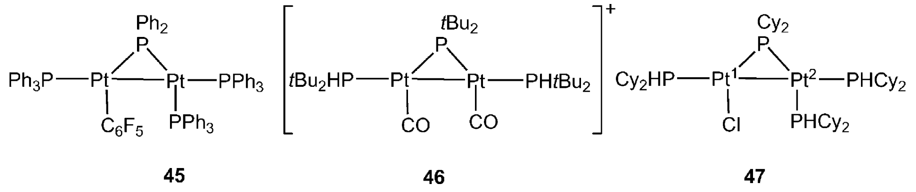


Figure 2. X-ray structures of complexes **37a** (left) and **39** (right).



Scheme 8. Mixed bridge Pt^{I} systems.



Scheme 9. Monobridged Pt^{I} complexes.

bornene)$_2$]$^+$*(Pt–Pt)* (**43**)[42] (Scheme 8) form: the first by fragmentation of a triangulo Pt$_3$ cluster, the second by treatment of [Pt$_2$(μ-dppm)$_2$Cl$_2$] with norbornene and AgOTf. Complex {(PPh$_3$)Pt{μ-C$_6$H$_4$(PPh$_2$)-2}}(μ-PPh$_2$)Pt-(PPh$_3$)]*(Pt–Pt)* (**44**), containing an *ortho*-metallated triphenylphosphane group bridging the Pt^{I}–Pt^{I} bond, is a product of thermolysis of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)][43] and adds electrophilic metal reagents [M(PPh$_3$)]$^+$ (M = Cu, Ag, Au) at the metal–metal bond.[44]

Scheme 9 shows the dinuclear Pt^{I} complexes [(PPh$_3$)-(C$_6$F$_5$)Pt(μ-PPh$_2$)Pt(PPh$_3$)$_2$]*(Pt–Pt)* (**45**),[45] [(PH*t*Bu$_2$)-(CO)Pt(μ-P*t*Bu$_2$)Pt(PH*t*Bu$_2$)(CO)]$^+$*(Pt–Pt)* (**46**)[46] and [(PHCy$_2$)(Cl)Pt(μ-PCy$_2$)Pt(PHCy$_2$)$_2$]*(Pt–Pt)* (**47**),[34] in which the metals are linked by only one phosphanido bridge. Complex **47** was obtained, as a minor product, by sodium reduction of **36** at low temperature. Because of the crowding in the coordination sphere of Pt^2, the rotation of the PHCy$_2$ ligands about the P–Pt^2 bonds are hindered at room temperature.[34]

In Table 2 are collected structural features and ^{195}Pt NMR spectroscopic data for selected phosphanido-bridged Pt^{I} compounds. The Pt–Pt distances (2.6–2.7 Å) are compatible with a single metal–metal bond. The ^{195}Pt chemical shifts fall mostly between –5000 and –5600 ppm; exceptions are represented by the C- or O-bonded ^{195}Pt atoms in **35**, **39** and **44** that resonate in the region between –4400 and –4800 ppm.

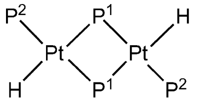
Table 2. Pt–Pt interatomic distances and ^{195}Pt NMR chemical shifts for selected phosphanido-bridged Pt^{I}–Pt^{I} complexes.

	$d_{Pt–Pt}$ [Å]	$\delta_{Pt(1)}$ [ppm]	$\delta_{Pt(2)}$ [ppm]	Ref.
28	2.604(1)	[a]		[36]
31	[a]	–5514		[34]
32	2.6127(6)	–5483	–5220	[7]
34b	[a]	–5177		[38]
35	2.5980(3)	–4929	–4523	[38]
37a	2.6307(5)	–5570		[39]
38a	[a]	–5530	–5570	[39]
39	2.5731(16)	–4798	–5205	[40]
41	[a]	–5218	–5376	[40]
43	2.7047(6)	–5786		[42]
44	2.657(1)	–4452	–4948	[44]
46	2.6743(5)	–5429	–5429	[46]

[a] Not given.

3.2. Hydrido Complexes

The terminal hydrido complex *anti*-[(PEt$_3$)(H)Pt(μ-PPh$_2$)]$_2$ (**48**, Scheme 10), originally obtained by addition of PHPh$_2$ and NaOEt to *trans*-[Pt(H)(Cl)(PEt$_3$)$_2$],[17] was prepared also by treatment of *trans*-[Pt(H)(Cl)(PEt$_3$)$_2$] with SiMe$_3$(PPh$_2$)[47] or by reaction of PHPh$_2$ with an equimolar amount of [Pt(PEt$_3$)$_3$].[48] In the latter case, the formation of a mixture of the *anti* and *syn* isomers was indicated by ^{1}H NMR spectroscopy. Complexes *anti*-[(PEt$_3$)(H)Pt(μ-P*t*Bu$_2$)]$_2$ (**49**) and *anti*-[(PH*t*Bu$_2$)(H)Pt(μ-P*t*Bu$_2$)]$_2$ (**50**), having related structures, were obtained by reaction of PH*t*Bu$_2$ with [Pt(PEt$_3$)$_3$][48] and [(η^5-Cp)Pt(η^3-C$_3$H$_5$)],[49] respectively.

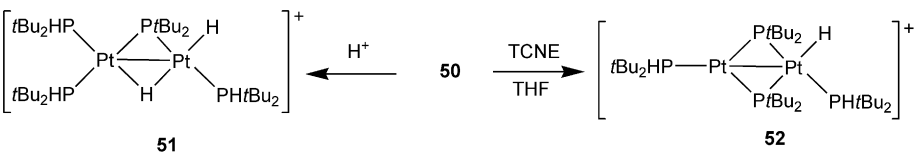


48 P^1 = PPh$_2$, P^2 = PEt$_3$
49 P^1 = P*t*Bu$_2$, P^2 = PEt$_3$
50 P^1 = P*t*Bu$_2$, P^2 = PH*t*Bu$_2$

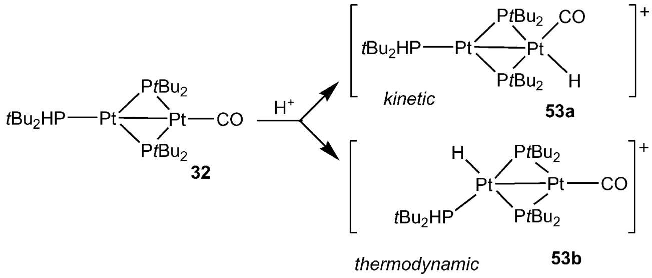
Scheme 10.

Protonation of **50** gives [(PH*t*Bu$_2$)$_2$Pt(μ-P*t*Bu$_2$)(μ-H)-Pt(H)(PH*t*Bu$_2$)]$^+$*(Pt–Pt)* (**51**), which contains a bridging phosphanide, a bridging hydride and a terminal hydride, while reaction with tetracyanoethylene (TCNE) in thf gives the bis(phosphanido) complex [(PH*t*Bu$_2$)Pt(μ-P*t*Bu$_2$)$_2$-Pt(H)(PH*t*Bu$_2$)]$^+$*(Pt–Pt)* (**52**) (Scheme 11).[50] Terminal hydrido complexes [Pt$_2$(μ-P*t*Bu$_2$)$_2$(PH*t*Bu$_2$)(CO)]$^+$*(Pt–Pt)* **53a**,**b** are obtained by protonation of the Pt^{I}–Pt^{I} monocarbonyl derivative **32**;[7] the first under kinetic, but the second under thermodynamic control (Scheme 12).[51]

Oxidative addition of a secondary phosphane may result in complexes containing μ-phosphido and terminal hydrido ligands. Complex *anti*-[(PPh$_3$)(C$_6$F$_5$)Pt(μ-PPh$_2$)$_2$Pt(H)-(PPh$_3$)] (**54**, Scheme 13) forms by an intermolecular reac-

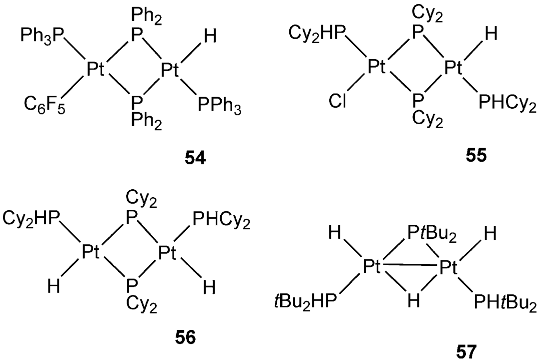


Scheme 11.



Scheme 12.

tion of **45** with $PHPh_2$,[45] whereas *anti*-[$(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)_2Pt(H)(PHCy_2)$] (**55**) is the product of intramolecular oxidative addition of a coordinated $PHCy_2$ of **47**.[34]

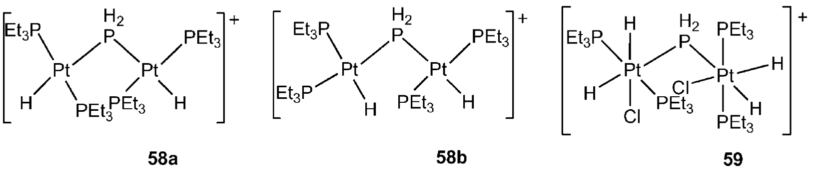


Scheme 13.

Moreover, the dihydride *syn*-[$(PHCy_2)(H)Pt(\mu\text{-}PCy_2)$]$_2$ (**56**), in the unusually *syn* geometry, is the major product of sodium reduction of *cis*-[$PtCl_2(PHCy_2)_2$] (**36**) at 0 °C (the other product being **47**),[34] whereas the trihydride *syn*-[$(H)(PHt\text{Bu}_2)Pt(\mu\text{-}Pt\text{Bu}_2)(\mu\text{-}H)Pt(H)(PHt\text{Bu}_2)$]*(Pt–Pt)* (**57**) forms by the $NaBH_4$ reduction of *trans*-[$PtCl_2(PHt\text{Bu}_2)_2$] carried out in presence of free $PHt\text{Bu}_2$.[52] Other examples of phosphanido-bridged diplatinum complexes containing terminal hydrides are the cations [$(PEt_3)_2(H)Pt(\mu\text{-}PH_2)Pt(H)(PEt_3)_2$]$^+$ (**58a**,**b**) and [$(PEt_3)_2(H)_2(Cl)Pt(\mu\text{-}PH_2)Pt(H)_2(Cl)(PEt_3)_2$]$^+$ (**59**),[53,54] the latter being the only known phosphanido-bridged platinum complex in which the formal oxidation state of the metal is +4 (Scheme 14).

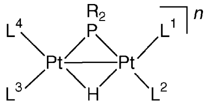
An interesting class of Pt phosphanides is represented by complexes featuring the $Pt_2(\mu\text{-}H)(\mu\text{-}PR_2)$*(Pt–Pt)* core (**51**, **57**, **60**–**76**, Table 3). All of these complexes, in which the metals are in a formal oxidation state of +2, present a valence electron count of 30, thus requiring a single bond between the Pt atoms. The cyclic Pt_2H fragment can be represented by a three-centre, two-electron (3 c, 2 e) system, the bridging hydrogen atom having an intermediate behaviour between that of a proton and of a hydrido ligand.[40] This is in agreement with: (i) the relatively short Pt–Pt bond length found for these complexes, in which the Pt–Pt bond is not yet completely broken as expected for a "true" Pt^{II}–Pt^{II} system, (ii) the acidity of the bridging hydride, attested by the ease of deprotonation proven for some of these compounds.[55] The Pt–Pt bond lengths range from 2.8239 Å to 2.912 Å and are ca. 0.2 Å longer than those found for Pt^I–Pt^I dimers. In the ^{31}P NMR spectra the μ-P is deshielded (the chemical shifts range from 100 to 214 ppm) as expected for bridging phosphanides subtending a metal–metal bond. The bridging hydride ^1H NMR resonances fall, at high field, between –4 and –9 ppm. Finally, the ^{195}Pt NMR chemical shifts are in the same region as those of Pt^I–Pt^I dimers (comparison of Table 2 and Table 3).

Complex [$(PPh_3)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(Ph)(PPh_3)$]$^+$*(Pt–Pt)* (**60**) was first obtained by reaction of [$Pt(cod)_2$] with *trans*-[$Pt(Ph)(acetone)(PPh_3)_2$]BF_4, PPh_3 and H_2[56] and is also the decomposition product of *trans*-[$(PPh_3)_2Pt(H)(thf)$]$^+HC(SO_2CF_3)_2^-$.[57] Decomposition of [$Pt(H)\{CH_2C(Me_2)P(t\text{Bu})_2\}(PPh_3)$] results in the formation of complex *syn*-[$(H)(PPh_3)Pt(\mu\text{-}Pt\text{Bu}_2)(\mu\text{-}H)Pt\{CH_2C(Me_2)P(t\text{Bu})_2\}$]*(Pt–Pt)* (**61**).[58] One of the inactive complexes arising upon prolonged hydroformylation reactions catalysed by [$Pt\{(PPh_2O)_2H\}(H)(PPh_3)$] is the dimer [$(PPh_2OH)(PPh_2O)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_2OH)(PPh_2O)$]*(Pt–Pt)* (**62**).[59] Complex [$(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PHPh_2)(PPh_3)$]*(Pt–Pt)* (**63**) is obtained from reactions of *cis*-[$Pt(C_6F_5)_2(PHPh_2)_2$] with [$Pt(norbornene)_3$] and PPh_3.[45] The alkynyl complex [$(PHt\text{Bu}_2)(PhC_2)Pt(\mu\text{-}Pt\text{Bu}_2)(\mu\text{-}H)Pt(PHt\text{Bu}_2)(CO)$]$^+$*(Pt–Pt)* (**64**) is produced by the reaction of **53b** with phenylacetylene.[60] Bridging hydrides resulting from protonation of the Pt^I–Pt^I bond are obtained upon treatment of **53a** with triflic acid {complex [$(PHt\text{Bu}_2)$-



Scheme 14.

Table 3. Pt–Pt interatomic distances and NMR spectroscopic parameters for complexes having the $Pt_2(\mu\text{-}H)(\mu\text{-}PR_2)$*(Pt–Pt)* core.



	R	L¹	L²	L³	L⁴	*n*	d_{Pt-Pt} [Å]	$\delta_{\mu P}$ [ppm]	$\delta_{\mu H}$ [ppm]	δ_{Pt} [ppm]	Ref.
57	*t*Bu	H	$PHtBu_2$	$PHtBu_2$	H	0	[a]	188.0	–6.22	–5995	[52]
60	Ph	Ph	PPh_3	PPh_3	PPh_3	+1	2.889(2)[b] 2.912(2)[b]	121.3	–6.5	–5641 –5349	[56]
61	*t*Bu	[c]	[c]	PPh_3	H	0	[a]	159.9	–6.61	[a]	[58]
62	Ph	$P(OH)Ph_2$	$P(O)Ph_2$	$P(O)Ph_2$	$P(OH)Ph_2$	0	2.907	99.5	–5.58	[a]	[59]
51	*t*Bu	H	$PHtBu_2$	$PHtBu_2$	$PHtBu_2$	+1	[a]	196.4	–7.34	[a]	[49]
63	Ph	$PHPh_2$	PPh_3	C_6F_5	C_6F_5	0	[a]	111.5	–6.0	[a]	[45]
64	*t*Bu	$PHtBu_2$	Ph–C≡C-	$PHtBu_2$	CO	+1	[a]	212.3	–5.1	–5559 –5677	[60]
65	*t*Bu	CO	$PHtBu_2$		$PHtBu_2$	+2	[a]	214	–5.9	–5564 –5205	[51]
66	Ph	PPh_3	PPh_3	CH_2Cl_2	PPh_3	+2	[a]	113.8	–5.44	[a]	[61]
67	Cy	$PHCy_2$	$P(O)Cy_2$	Cl	$PHCy_2$	0	[a]	145.2	–4.73	–5365 –5547	[55]
68	Cy	$PHCy_2$	$P(O)Cy_2$	Br	$PHCy_2$	0	[a]	151.1	–4.63	–5507 –5568	[55]
69	Cy	$PHCy_2$	$P(OH)Cy_2$	Cl	$PHCy_2$	+1	2.8778(15)	155.3	–5.61	–5379 –5621	[55]
70	Cy	$PHCy_2$	$P(OH)Cy_2$	Br	$PHCy_2$	+1	2.8379(4)	161.7	–5.51	–5522 –5638	[55]
71	Cy	$PHCy_2$	$P(O)Cy_2$	PhO	$PHCy_2$	0	[a]	124.9	–4.97	–5177 –5497	[55]
72	Cy	$PHCy_2$	$P(O)Cy_2$	CF_3CH_2O	$PHCy_2$	0	[a]	143.2	–4.32	–5358 –5585	[55]
73	Cy	$PHCy_2$	$P(O)Cy_2$	$P(O)Cy_2$	$PHCy_2$	0	2.8502(6)	125.0	–5.06	–5464	[40]
74	Cy	$PHCy_2$	$P(OH)Cy_2$	CH_3CN	$PHCy_2$	+2	2.8239(4)	155.2	–6.48	–5510 –5653	[62]
75	Cy	I	$PHCy_2$	I	$PHCy_2$	0	[a]	185.7	–7.29	–5723 –5550	[55]
76	Cy	PhS	$PHCy_2$	PhS	$PHCy_2$	0	[a]	154.1	–8.81	–5432 –5465	[55]

[a] Not given. [b] For the two independent molecules in the unit cell. [c] L^1^L^2 = $CH_2C(Me_2)PtBu_2$.

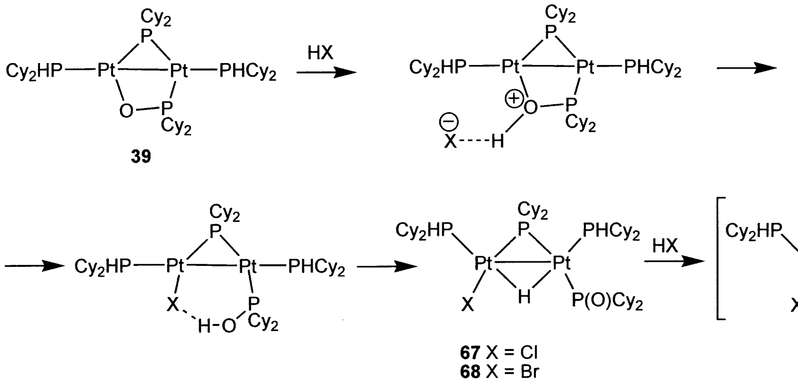
$(CO)Pt(\mu\text{-}PtBu_2)(\mu\text{-}H)Pt(PHtBu_2)]^{2+}$*(Pt–Pt)* (**65**)}[51] or by action of 2 equiv. HBF_4 on **44** in dichloromethane {complex $[(PPh_3)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(CH_2Cl_2)(PPh_3)]^{2+}$-*(Pt–Pt)* (**66**)}.[61]

Protonation of the μ-phosphinito complex **39** with strong acids such as HCl or HBr affords the neutral compounds *syn*-$[(PHCy_2)(X)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(O)Cy_2\}]$-*(Pt–Pt)* (**67**, X = Cl) or **68** (X = Br) respectively, when only 1 equiv. HX is uptaken. The cationic species *syn*-$[(PHCy_2)(X)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(OH)Cy_2\}]^+$*(Pt–Pt)* (**69**, X = Cl and **70**, X = Br) are obtained when **39** is treated with excess (> 2 equiv.) acid.[55] Neutral complexes analogous to **67** are obtained upon protonation of **39** by weak acids such as PhOH {to give *syn*-$[(PHCy_2)(PhO)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(O)Cy_2\}]$*(Pt–Pt)* (**71**)}, CF_3CH_2OH {to give *syn*-$[(PHCy_2)(CF_3CH_2O)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(O)Cy_2\}]$*(Pt–Pt)* (**72**)},[55] and $PH(O)Cy_2$ {to give *syn*-$[(PHCy_2)\{P(O)Cy_2\}Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(O)Cy_2\}]$*(Pt–Pt)* (**73**)}. In the latter case the tautomeric pyramidal form $P(OH)Cy_2$ (dicyclohexylphosphinic acid) is held responsible for the formation of the symmetric complex **73**.[40]

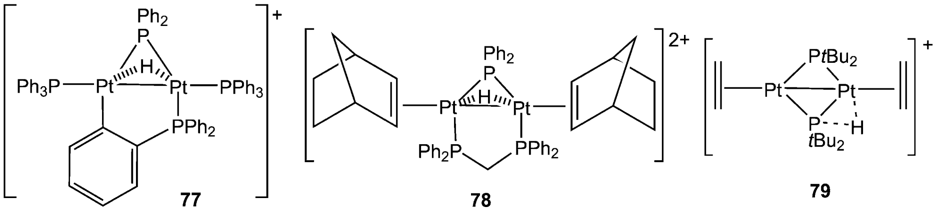
The solvento species *syn*-$[(PHCy_2)(CH_3CN)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)\{P(OH)Cy_2\}]^{2+}$*(Pt–Pt)* (**74**) is obtained when **39** is reacted with HBF_4, a Brønsted acid having a weakly coordinating anion.[62] When **39** reacts with HI or PhSH, the final products are the complexes *anti*-$[(PHCy_2)(X)Pt(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(PHCy_2)(X)]$*(Pt–Pt)* (X = I, **75** or X = PhS, **76**) deriving from substitution of an iodide (or thiophenoxide) group for the $P(O)Cy_2$ ligand, as a result of the high affinity of S and I towards Pt, in view of their "soft" character.[55]

Multinuclear NMR spectroscopic and DFT studies on the protonation of **39** by strong hydrohalic acids allowed the elucidation of the mechanism outlined in Scheme 15, where the HX first protonates the phosphinito oxygen, giving a six membered platinacycle that transforms into the bridging hydride species **67**–**70**.

The uptake of only 1 equiv. H^+ by **44** gives complex $[\{(PPh_3)Pt\{\mu\text{-}C_6H_4(PPh_2)\text{-}2\}PPh_2\}(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)]^+$-*(Pt–Pt)* (**77**), where the hydride forms a third bridge between the Pt atoms.[61] The related complex $[Pt_2(\mu\text{-}PPh_2)(\mu\text{-}dppm)(\mu\text{-}H)(norbornene)_2]^{2+}$*(Pt–Pt)* (**78**) is obtained by protonation of **43** by TfOH.[63] For **78** a fast intramolecular



Scheme 15. Mechanism of protonation of complex **39** by HX (X = Cl, Br).

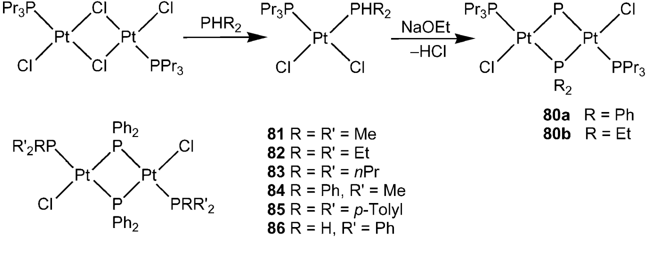


Scheme 16.

inversion of the hydride is suggested to explain the equivalence of the dppm-methylene hydrogen atoms.[63] Finally, the adduct $[Pt_2(\mu\text{-}PtBu_2)(\mu\text{-}PHtBu_2)(\eta^2\text{-}CH_2{=}CH_2)_2]^+$ (**79**, Scheme 16), formed by protonation of $[Pt(\mu\text{-}PtBu_2)(\eta^2\text{-}CH_2{=}CH_2)_2]_2$, contains a rarely observed P–H–M agostic proton in rapid exchange with those of the adjacent ethylene molecule and represents an example of proton attack onto the Pt–μ–P bond.[64]

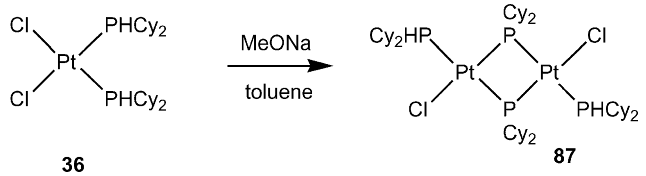
3.3. Halido Complexes

The synthetic procedures employed by Chatt and Davidson for obtaining the chlorido complexes *anti*-$[(PnPr_3)(Cl)Pt(\mu\text{-}PR_2)]_2$ (**80**) are outlined in Scheme 17 and comprise, first, the bridge splitting in dichlorido-bridged precursors by a secondary phosphane, and then the base-facilitated dehydrochlorination of the mononuclear chlorido complexes obtained.[17]



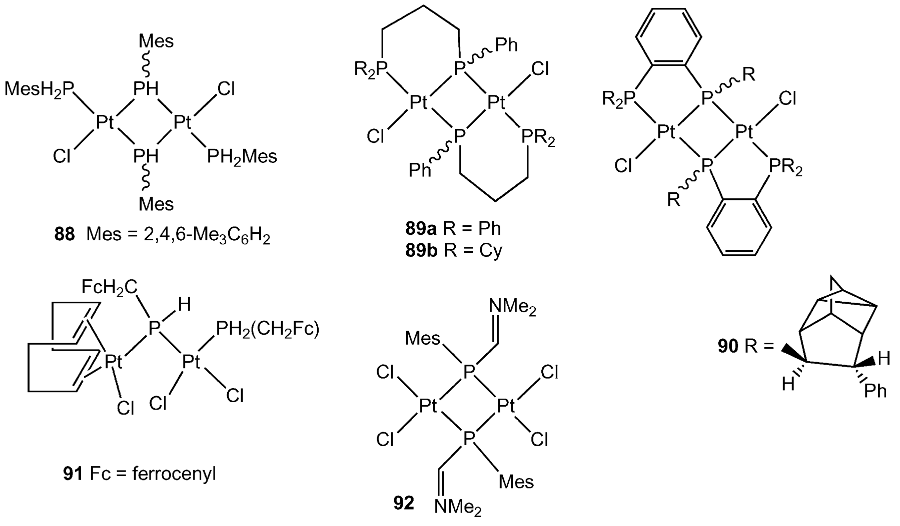
Scheme 17. Diethyl- and diphenylphosphanido Pt^{II} chlorides.

Compounds *anti*-$[(PRR'_2)(Cl)Pt(\mu\text{-}PPh_2)]_2$ (**81**–**85**) having the same structure as **80** are obtained: (i) from suitable (tetrachlorido)platinum(II) dimers by reaction with $(Me_3Si)PPh_2$[47] (**81**–**84**), (ii) by reaction of $Ph_2P\text{–}P(SiMe_3)_2$ with $[PtCl_2(p\text{-}Tol_3P)_2]$ (**85**),[65] (iii) by reaction of a platinum(II) chloride $\{PtCl_2$,[66] $PtCl_2(PhCN)_2$[67] or $K_2PtCl_4\}$[68] with $PHPh_2$ in refluxing benzene (**86**). Although the latter procedure did not hold for $PHCy_2$,[69] the dicyclohexylphosphanido-bridged complex *anti*-$[(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)]_2$ (**87**) could be obtained by base-facilitated dehydrochlorination of **36** in toluene (Scheme 18).[39]



Scheme 18.

Chlorido complexes containing asymmetric phosphanido P atoms are obtained with primary phosphanido groups {as in the case of *anti*-$[(PH_2Mes)(Cl)Pt(\mu\text{-}PHMes)]_2$ (**88**)}[70] or when the bridging phosphanide is incorporated into a chelate ring $\{[PtCl\{PhP(CH_2)_3PR_2\}]_2$ (**89**)[71] and $[PtCl\{(+)_\delta\text{-}L\}]_2$ (**90**), L = deprotonated form of *P,P,P'*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene[72]} (Scheme 19). As a result of the presence of two stereogenic phosphanido units, three isomers are possible: two chiral and one *meso*. For complex **89b** it has been found that in the chiral diplatinum molecule the tetraatomic Pt_2P_2 core is bent, whereas in the *meso* species the tetraatomic Pt_2P_2 core is planar. A planar Pt_2P_2 core has been found also for complexes **84**,[68] **85**[73] and **88**.[70]

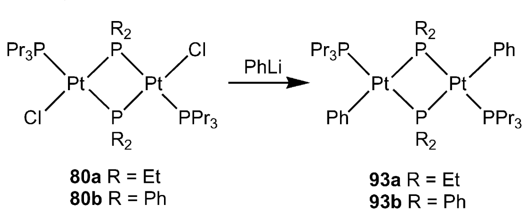


Scheme 19.

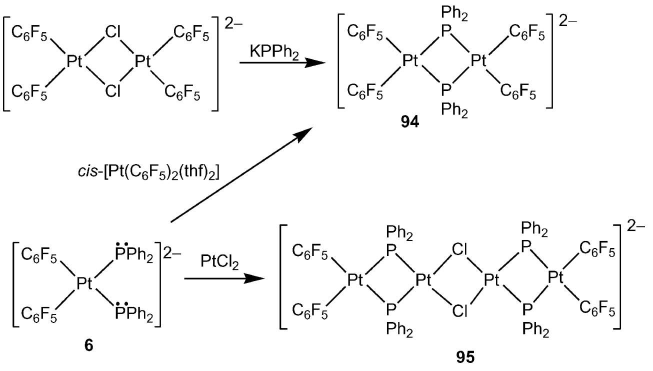
The trichlorido compound $[(cod)(Cl)Pt(\mu\text{-}PHCH_2Fc)\text{-}Pt(Cl)_2(PH_2Fc)]_2$ (**91**, Fc = ferrocenyl) seems to be the only existing example of a monobridged primary phosphanide Pt_2 complex,[74] while the tetrachloride species $[PtCl_2\{\mu\text{-}MesP{=}CH(NMe_2)\}]_2$ (**92**) features the behaviour of the phosphaalkene ligand as a pseudozwitterionic moiety (P^-~N^+,[75] Scheme 19).

3.4. Aryl or Alkyl Complexes

Organometallic compounds *anti*-$[(PnPr_3)(Ph)Pt(\mu\text{-}PR_2)]_2$ (**93**) were obtained by reaction of the corresponding terminal chlorides **80** with PhLi or PhMgBr (R = Ph, Scheme 20) or by substitution of bridging bromides for bridging phosphanides of suitable precursors, by reaction with PR_2Li (R = Ph, Et).[17] The latter reaction has been exploited by Forniés for the synthesis of the pentafluorophenyl derivative $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)]_2$ (**94**), which can also be prepared by reaction of **6** with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (Scheme 21).[22]



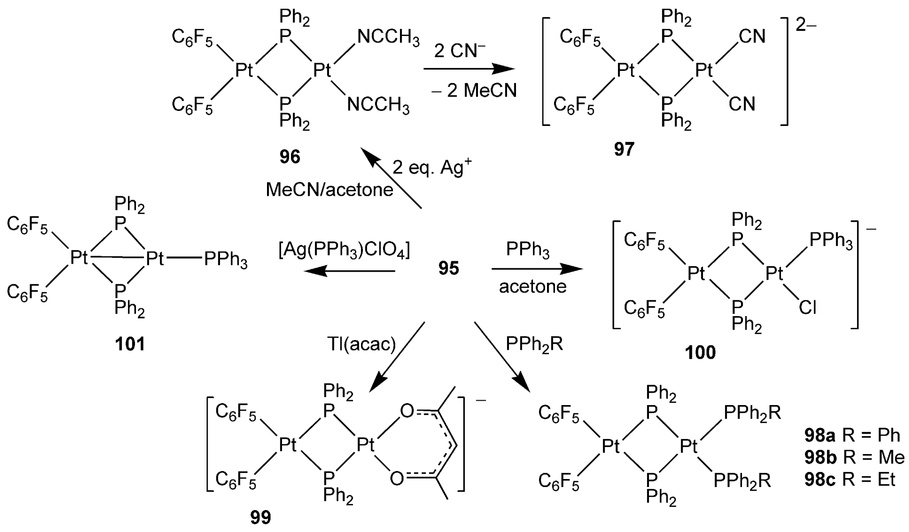
Scheme 20.



Scheme 21.

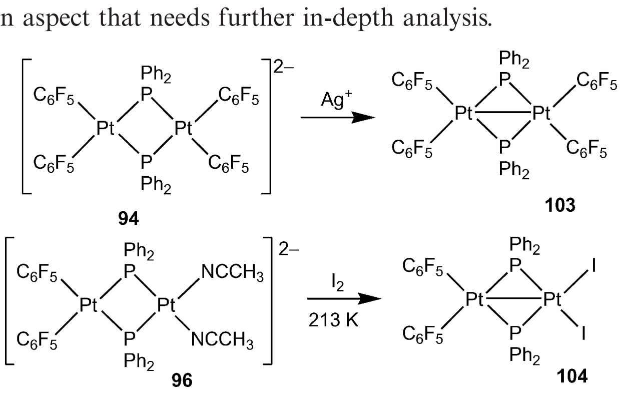
When **6** is reacted with $PtCl_2$, the tetranuclear compound $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)]_2$ (**95**) is obtained, which proved to be a precursor of several phosphanido-bridged di- and polynuclear compounds as well as of the bis(acetonitrile) complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(CH_3CN)_2]$ (**96**), which, in turn, gives the bis(cyano) complex $[(C_6F_5)_2\text{-}Pt(\mu\text{-}PPh_2)_2Pt(CN)_2]^{2-}$ (**97**) by ligand substitution (Scheme 22).[76] The organometallic phosphanido-bridged dinuclear compounds originating from **95** are shown in Scheme 22. The addition of excess phosphane PPh_2R (R = Ph, Me, Et) to **95** in CH_2Cl_2/MeOH gave the neutral compounds $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_2R)_2]$ (**98**), whereas the acetylacetonato complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(acac)]^-$ (**99**) forms from **95** and Tl(acac).[77] Reaction of **95** with PPh_3 in acetone yields $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)(Cl)]^-$ (**100**), while reaction of **95** with $[Ag(PPh_3)ClO_4]$ gives the unsaturated species $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PPh_3)]$*(Pt–Pt)* (**101**) containing a dative Pt→Pt bond.[78] The structurally related complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}Ph)Pt(PPh_3)]$*(Pt–Pt)* (**102**) is one of the products obtained from reactions of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ with $[Pt(\eta^2\text{-}alk)(PPh_3)_2]$ (alk = $H_2C{=}CH_2$, $HC{\equiv}CSiMe_3$ or $HC{\equiv}CtBu$).[79]

Dinuclear complexes in which the Pt atoms exhibit a formal oxidation state of +3 have been obtained by Forniés from reactions of dimeric complexes with oxidants. The reaction of **94** with Ag^+ affords selectively the neutral complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)]_2$*(Pt–Pt)* (**103**),[80] while iodine addition to **96** at low temperature gives the diiodido species $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PtI_2]$*(Pt–Pt)* (**104**, Scheme 23). The oxidised species have the metal centres in square-planar coordination environments involving a coplanar Pt^{III}–Pt^{III} bond.[81] Interestingly, the ^{195}Pt NMR chemical shift values found for **94** (δ = –3795) and **103** (δ = –5298)[82] indicate



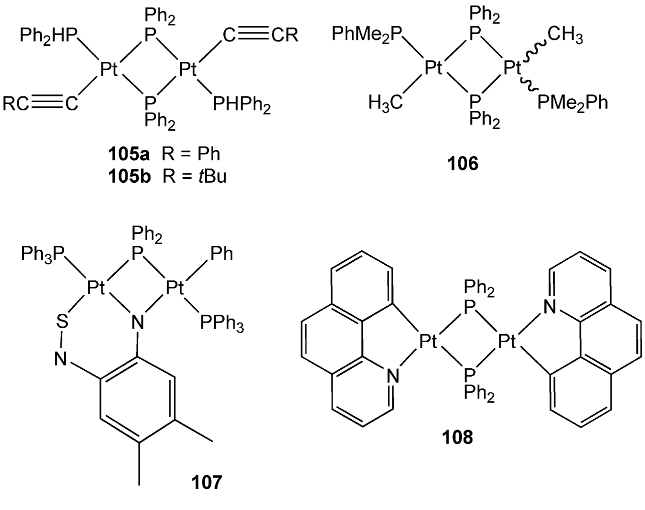
Scheme 22. Reactivity of the tetranuclear compound **95**.

that for square planar Pt^{III} complexes the increase in oxidation state results in a strong shielding of the ^{195}Pt nuclei, an aspect that needs further in-depth analysis.



Scheme 23. Synthesis of dinuclear Pt^{III} compounds.

The alkynyl complexes *anti*-$[(PHPh_2)(RC{\equiv}C)Pt(\mu\text{-}PPh_2)]_2$ (R = Ph, **105a**; R = *t*Bu, **105b**) are obtained as byproducts, the first by addition of $PHPh_2$ to a mixture of $[PtCl_2(tht)]$ and $LiC{\equiv}CPh$, and the second from reaction of *cis*-$[Pt(C{\equiv}C\mathit{t}Bu)_2(cod)]$ with $PHPh_2$.[83] The methylplatinum dimer $[(Me)(PMe_2Ph)Pt(\mu\text{-}PPh_2)]_2$ (**106**) is formed by reaction of *cis*-$[Pt(Me)_2(PMe_2Ph)_2]$ with $PHPh_2$.[84] The phenylplatinum complex $[Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph]$ (**107**) is obtained from reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with 5,6-dimethyl-2,1,3-benzothiadiazole (Scheme 24).[85] The 7,8-benzoquinolinate complex $[Pt(bzq)(\mu\text{-}PPh_2)]_2$ (**108**) forms when $[Pt(bzq)(\mu\text{-}Cl)]_2$ reacts with $PHPh_2$ and Et_3N (Scheme 24).[86]

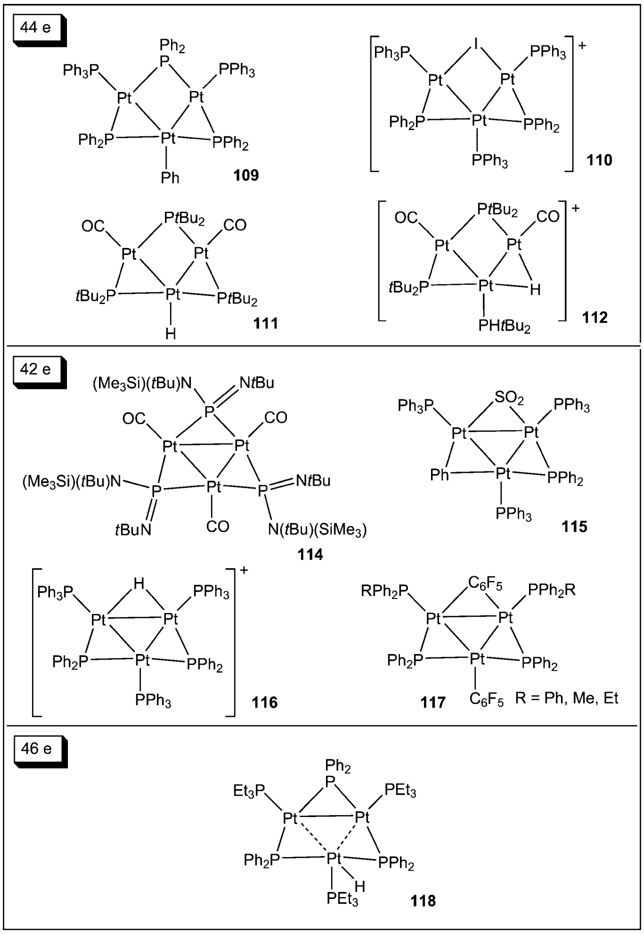


Scheme 24.

4. Phosphanido-Bridged Polynuclear Platinum Complexes

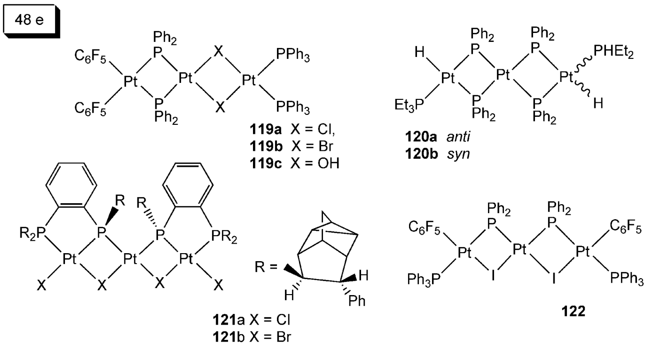
The known triplatinum species with bridging phosphanido ligands have three structures: triangular, linear and bent. Depending on the valence electron count, they exhibit zero (48 e), one (46 e), two (44 e) or three (only for triangular compounds with 42 valence electrons) Pt–Pt bonds. A selection of triangulo Pt_3 clusters with their valence electron count is shown in Scheme 25. Cluster $[Pt_3(\mu\text{-}PPh_2)_2Ph(PPh_3)_2]$ (**109**)[36] exists in two structural isomeric forms that differ essentially in their metal–metal distances and Pt–μP–Pt angles.[87] It reacts with I_2 by recombination of a PPh_2 bridge and a terminal Ph group to form the cationic iodido-bridged cluster $[Pt_3(\mu\text{-}I)(\mu\text{-}PPh_2)_2(PPh_3)_3]^+$ (**110**).[88] The cluster $[Pt_3(\mu\text{-}P\mathit{t}Bu_2)_3(H)(CO)_2]$ (**111**), its protonated form $[Pt_3(\mu\text{-}P\mathit{t}Bu_2)_2(\mu\text{-}H)(PH\mathit{t}Bu_2)(CO)_2]^+$ (**112**)[89] as well as the species obtained by substitution of the terminal hydride in **111** by neutral or anionic ligands[90] are further examples of 44 e triangulo derivatives, in which the Pt atoms exhibit the formal oxidation states +1, +1, +2. The protonation of **111** carried out in the presence of CO and in an excess of acid gives $[Pt_6(\mu\text{-}P\mathit{t}Bu_2)_4(CO)_6]^{2+}$ (**113**),[91] a rare example of a hexanuclear phosphanido Pt cluster. The class of 42 e phosphanido-bridged Pt_3 triangulo clusters is represented by $[Pt_3\{\mu\text{-}(SiMe_3)(\mathit{t}Bu)N\text{–}P{=}N\mathit{t}Bu\}_3(CO)_3]$

(**114**),[92] $[Pt_3(\mu\text{-}PPh_2)(\mu\text{-}Ph)(\mu\text{-}SO_2)(PPh_3)_3]$ (**115**),[93] $[Pt_3(\mu\text{-}PPh_2)_2(\mu\text{-}H)\{(PPh_3)_3\}]^+$ (**116**)[94] and $[Pt_3(\mu\text{-}PPh_2)_2(\mu\text{-}C_6F_5)(PPh_2R)_2(C_6F_5)]$ (**117**),[77] whereas $[Pt_3(\mu\text{-}PPh_2)_3(H)(PEt_3)_3]$ (**118**) has a valence electron count of 46.[48] The terminal hydride in **118** is readily cleaved out by arylboronic acid, MeI and CuI.[48]

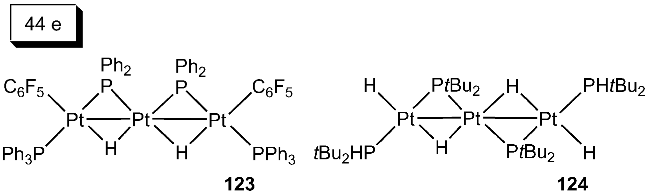


Scheme 25. Triangular Pt_3 clusters.

Compounds $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}X)_2Pt(PPh_3)_2]$ (**119**),[95] $[(H)(PEt_3)Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(H)(PEt_3)]$ (**120**),[48] $[Pt_3X_4\{(+)_\delta\text{-}L\}_2]$ {X = Cl, Br; L = deprotonated form of *P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)-benzene} (**121**)[72] and $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)Pt(PPh_3)(C_6F_5)]$ (**122**)[96] (Scheme 26) are linear triplatinum species not containing Pt–Pt bonds, whereas $[(C_6F_5)(PPh_3)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)(C_6F_5)]$ (**123**) and $[(H)(PHtBu_2)Pt(\mu\text{-}PtBu_2)(\mu\text{-}H)Pt(\mu\text{-}PtBu_2)(\mu\text{-}H)Pt(H)(PHtBu_2)]$ (**124**) are polyhydridic species endowed with two Pt–Pt bonds (Scheme 27). Dihydride **123** forms together with **63**,[45] whereas tetrahydride **124** is obtained, after work-up, by $NaBH_4$ reduction of *trans*-$[PtCl_2(PHtBu_2)_2]$.[97] Oxidation of the 48 e trimer $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^{2-}$ (**125**) yields the 46 e species $[(C_6F_5)_2Pt^1(\mu\text{-}PPh_2)_2Pt^2(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2](Pt^1\text{–}Pt^2)$ (**126**) for which a dynamic process renders equivalent the pentafluorophenyl groups in solution at room temperature.[98] Reaction of **126** with NBu_4Br or I^- results in the formation of $[(C_6F_5)\{PPh_2(C_6F_5)\}Pt(\mu\text{-}PPh_2)(\mu\text{-}X)Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]^-$ (**127a**,**b**) through an intramolecular PPh_2/C_6F_5 reductive coupling and the formation of the phosphane $PPh_2(C_6F_5)$ (Scheme 28).[99] A similar process was found to be operative (i) upon prolonged stirring of **104**,[81] (ii) when $AgClO_4$ was treated with 2 equiv. $[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)\}_2]$ to form $[Pt_2Pd_2(\mu\text{-}PPh_2)_3(C_6F_5)_3(PPh_2C_6F_5)]$,[100] (iii) when **94** was treated with I_2.[101]

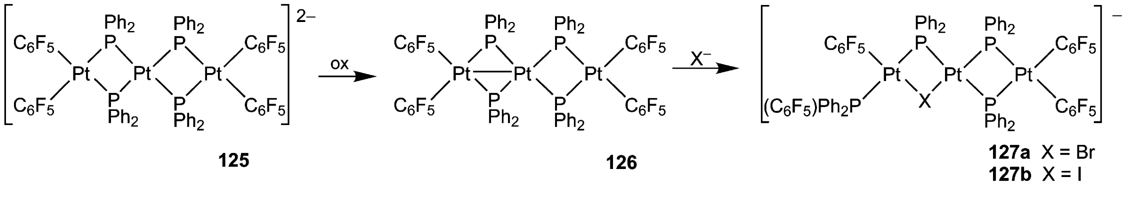


Scheme 26.

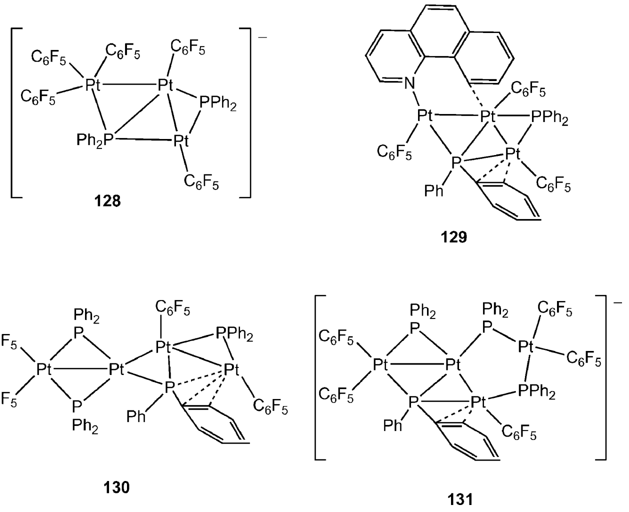


Scheme 27. Linear trinuclear Pt hydrides.

From the reaction of **95** with *cis*-$[Pt(C_6F_5)_2(thf)_2]$, the bent triplatinum species $[Pt_3(\mu\text{-}PPh_2)_2(C_6F_5)_5]^{2-}$ (**128**) forms, which contains a triply bridging diphenylphosphanido ligand acting as a 6 e donor.[102] Triply bridging PPh_2 are encountered also in $[Pt_3(bzq)(\mu\text{-}PPh_2)_2(C_6F_5)_3]$ (**129**)[103] and in the tetranuclear Pt complexes $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_4]$ (**130**)[104] and $[Pt_4(\mu\text{-}PPh_2)_4(C_6F_5)_5]^-$ (**131**)[105] (Scheme 29).

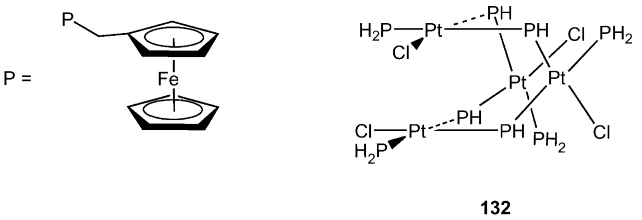


Scheme 28.



Scheme 29. Polynuclear complexes exhibiting triply bridged PPh_2 ligand.

While tetranuclear diphenylphosphanido-bridged Pt complexes invariably exhibit linear or bent disposition[106] of the Pt_4–μP_n motifs, when the bridging phosphanide is the deprotonated form of (ferrocenylmethyl)phosphane, the peculiar cyclic arrangement shown in Scheme 30 for $[Pt(PH_2CH_2Fc)Cl(\mu\text{-}PHCH_2Fc)]_4$ (**132**) is adopted.[107]

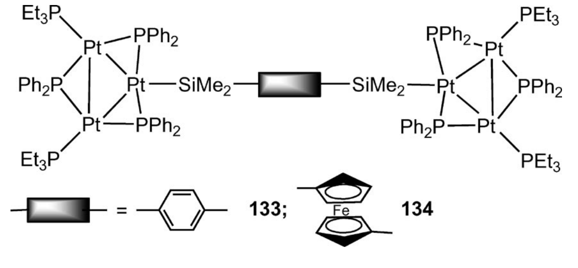


Scheme 30. The cyclic arrangement adopted by **132**.

5. Future Trends

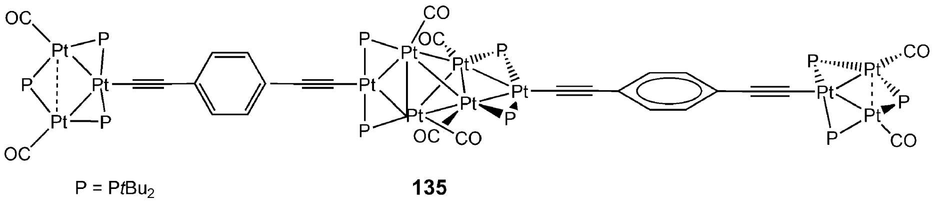
Two fields where (phosphanido)platinum compounds show promise are catalysis and materials science. As far as catalysis is concerned, a great impulse can be foreseen for the use of phosphanido complexes as precatalysts in industrial processes where the deactivation of the catalyst still represents a problem. The ability of phosphanido groups to bridge different metals to give heterodimetallic complexes (or clusters) allows one, in principle, to exploit possible cooperative effects of the adjacent metal centres in catalytic reactions.[108] Dinuclear phosphanido-bridged Pt complexes were proposed as intermediates in the hydrophosphination of acrylonitrile and *anti*-$[(PR_3)(H)Pt(\mu\text{-}PR_2)_2Pt(H)(PR_3)]$ (R = $-CH_2CH_2CN$, **133**) revealed to be catalytically active in the same reaction.[109] The bridging hydrido complex **60** was used by Parkins et al. as a precatalyst in the hydration of 1-octene.[110] Terminal phosphanido Pt complexes were suggested as intermediates in the catalysed addition of PH_3 to formaldehyde.[111] On the other hand, diastereomeric terminal phosphanido Pt complexes with chiral ancillary ligands were used in asymmetric hydrophosphination of acrylonitrile or related Michael acceptors and in asymmetric alkylation of secondary phosphanes.[112] For the latter reaction, high yields in PMe(Is)(CH_2Ph) and 70–77% *ee* were obtained when PHMe(Is) was treated with benzyl chloride (or bromide) in the presence of [Pt(*R*,*R*-Me-Duphos)-(Ph)(PMeIs)] (**17**).[25]

In the area of materials chemistry, the robustness of many phosphanido Pt complexes along with the tunability of their electronic properties by varying the ancillary ligands and/or oxidation states of the platinum atom render this class of compounds attractive for application in photophysics. In this regard, the emissive properties of the benzoquinolinatodiphenylphosphanido complex **108** (Scheme 24) have been recently studied.[86] Moreover, the controlled-nuclearity growth of complexes or clusters stabilised by phosphanido bridges paves the way to the assembly of large molecular frameworks with predefined shape. For instance, the cyano complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(CN)_2]^{2-}$ (**97**) acts a "metalloligand", giving the corresponding hexa- or octanuclear complexes by reaction with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ or $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(CH_3CN)_2]$ (**96**), respectively.[76] Other relevant examples are the hexanuclear complexes **133** and **134** composed of two cyclic triplatinum units connected with 1,4-phenylene or 1,1′-ferrocenylene spacers (Scheme 31).[113]



Scheme 31. Structure of hexanuclear complexes **133** and **134**.

Finally, interesting one-dimensional molecular architectures comprising (i) hexa- and trinuclear Pt clusters separated by conjugated 1,4-diethynylphenyl groups (**135**,



Scheme 32. 1-D chain structure of **135**.

Scheme 32)[114] or (ii) rigid-rod polymers with alternating hexanuclear clusters and conjugated spacers[115] were recently described.

6. Conclusions

(Phosphanido)platinum compounds exhibit a very rich chemistry, as the metal manifests five formal oxidation states (0, +1, +2, +3, +4, though only very few examples are reported for 0 and +4) and the phosphorus adopts the η^1, μ_2 and μ_3 coordination modes.

The terminally bonded phosphanide group shows no tendency to form multiple bonds with platinum. As a result, the lone pair on (pyramidal) P is highly nucleophilic, rendering it amenable to reaction with suitable metal fragments. This has been exploited for the synthesis of polynuclear species with diverse architecture by controlled-nuclearity growth. The nucleophilicity of the P lone pair is also responsible for the reactivity of terminal phosphanides with molecules such as O_2 and S_8.

Bridging phosphanides, thanks to their high flexibility and bridging ability, are ideal ligands for building polynuclear metal cores which remain stable during successive reactions. Nevertheless, the bridging phosphanide is not unreactive at all. There are examples where this ligand bridging two Pt atoms undergoes proton attack, reductive coupling or insertion reactions. Moreover, proton transfer from phosphorus in primary phosphanido (PHR) complexes yields phosphanylidene (PR) species, whose chemistry, in the case of platinum, is still little explored.[116]

Both terminal and bridging phosphanido complexes often arise upon activation of the P–H bond of primary or secondary phosphanes. The factors stabilising terminal vs. bridging coordination are not fully understood. In fact, according to Glueck, avoiding labile ligands such as halides and monodentate phosphanes is one way to favour the terminal coordination mode for the PPh_2^- ligand. However, *trans*-$[PtCl(PHCy_2)_2(PCy_2)]$ (**9**) is a stable complex, though it contains both monodentate (secondary) phosphanes and a chlorido ligand. Clearly, steric factors in addition to electronic ones must be taken into account.

Despite the extensive amount of data already collected in this field, the developments in phosphanido Pt (and other metals) chemistry will be in the fundamental coordination chemistry of such complexes, including theoretical and spectroscopic aspects. For instance, a deeper understanding on ring-size effect in the ^{195}Pt NMR spectroscopic features of the complexes[117] is necessary, in particular for three- and four-membered cycles.

The application of (phosphanido)platinum compounds in catalysis and materials science represents one of the most exciting challenge for chemical research in the field.

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