

Supplementary file

Structural Aspects of $\text{Pt}(\eta^3\text{-P}^1\text{C}_2\text{X}^1\text{C}_2\text{P}^2)(\text{Y})$ Derivatives-Types

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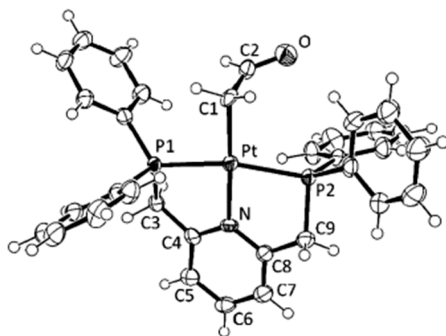
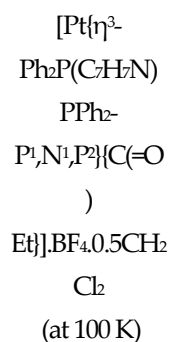
Table S1. Structures and applications of $\text{Pt}\{\eta^3\text{-P}^1\text{X}^1\text{P}^2\}(\text{Y})$, ($\text{X}^1=\text{O}^1, \text{N}^1$), ($\text{Y}=\text{C}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{P}^3\text{L}$) complexes

Table S2. Structures and applications of $\text{Pt}\{\eta^3\text{-P}^1\text{C}^1\text{P}^2\}(\text{Y})$, ($\text{Y}=\text{O}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{Cl}, \text{Br}$) complexes

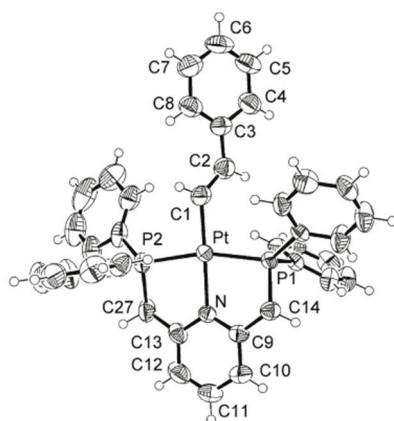
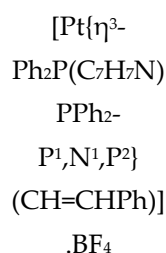
Table S3. Structures and applications of $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{S}^1$ or Si^1) ($\text{Y}=\text{C}^2\text{L}, \text{Cl}, \text{P}^3\text{L}, \text{I}, \text{H}, \text{O}^2\text{L}$) complexes

Table S1. Structures and applications of $\text{Pt}\{\eta^3\text{-P}^1\text{X}^1\text{P}^2\}(\text{Y})$, ($\text{X}^1=\text{O}^1, \text{N}^1$), ($\text{Y}=\text{C}^2\text{L}, \text{N}^2\text{L}, \text{Cl}, \text{P}^3\text{L}$) complexes^a

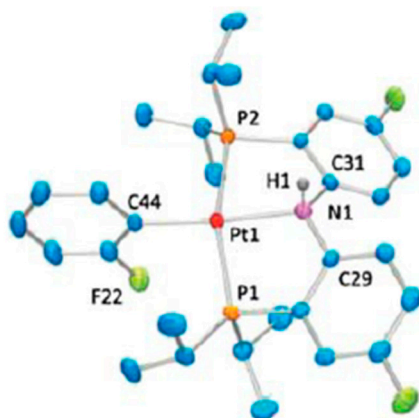
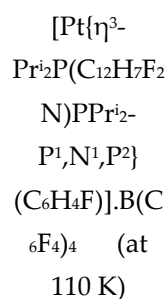
Complex	Structure	Application and Ref.
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{15}\text{H}_{12}\text{O})\text{PPh}_2\}\{\eta^1\text{-P}^3(\text{C}_5\text{H}_4\text{N})(\text{Ph})_2\}]\cdot 2\text{CF}_3\text{SO}_3\cdot 0.5\text{H}_2\text{O}$ (at 150 K)		reactivity of platinum complexes towards dihydrogen; platinum complexes react smoothly with dihydrogen under mild conditions to produce stable hydride complexes [19]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{12}\text{H}_8\text{N})\text{PPh}_2\}\{\eta^1, \text{N}^1, \text{P}^2\}(\text{py})\text{CF}_3\text{SO}_3\cdot \text{toluene}]$		the amido diphosphine complexes $[\text{PNP}]\text{PtMe}$ and $[\text{PNP}]\text{PtOTf}$, where $[\text{PNP}]_2$ is bis(2-diphenylphosphinophenyl)-amide effectively activate the benzene C–H bond in the presence of an appropriate Lewis acid or base, leading to the formation of $[\text{PNP}]\text{PtPh}$ quantitatively [20]
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_{12}\text{H}_8\text{N})\text{PPh}_2\}(\text{Cl})]\cdot 0.5\text{C}_6\text{H}_6$		



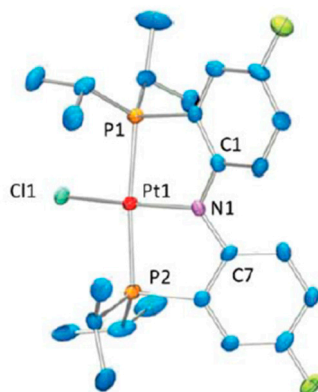
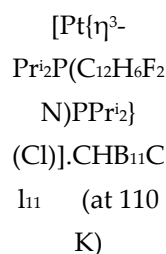
a dicationic platinum(II) complex providing water addition to alkynes; represents an innovative solution for the hydration of alkynes as an important reaction to synthesize aldehydes or ketones [22]

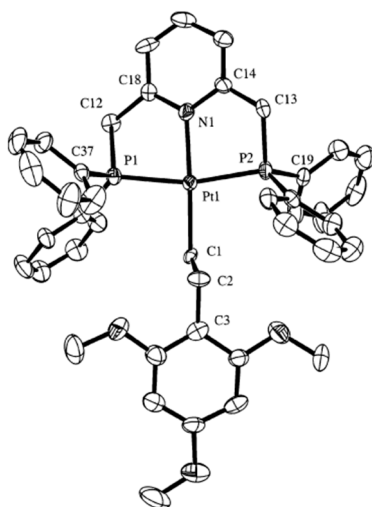
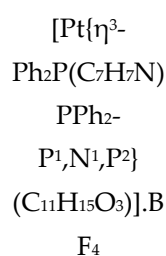


dicationic platinum(II) monoalkene complexes act in C-C, C-N, and C-O bond formations; vinylic deprotonation was observed with the platinum styrene complex [23]

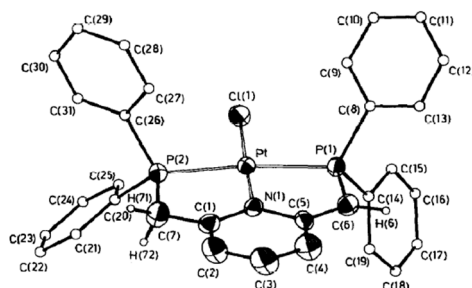
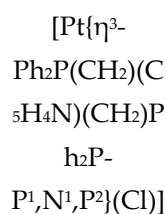


frustrated Lewis pair-like splitting of aromatic C-H bonds and abstraction of halogen atoms by a cationic [(FPNP)Pt]⁺ species [24]

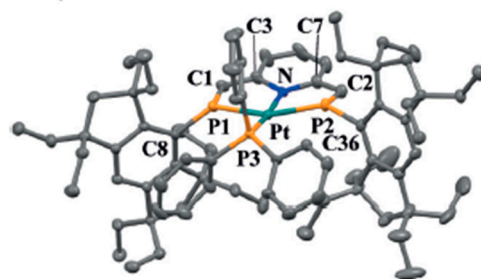
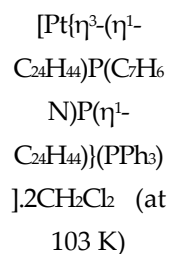




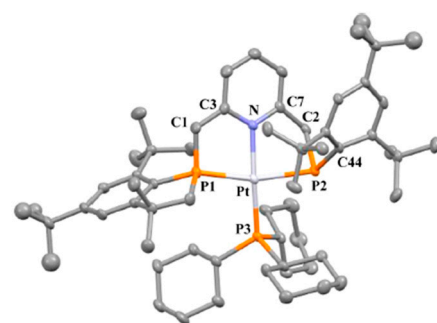
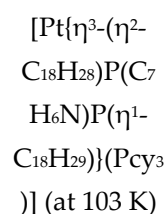
catalytic hydroarylation of
olefins is promoted by
dicationic
platinum(II) complexes; the
rates of C-C bond
formation and M-C
bond cleavage are inversely
correlated [25]



Study of structure and
mechanism of platinum(II)
complex formation with the
anionic terdentate ligand 2-
(CHPPh₂)-6-
(CH₂PPh₂)pyridine;
[27]

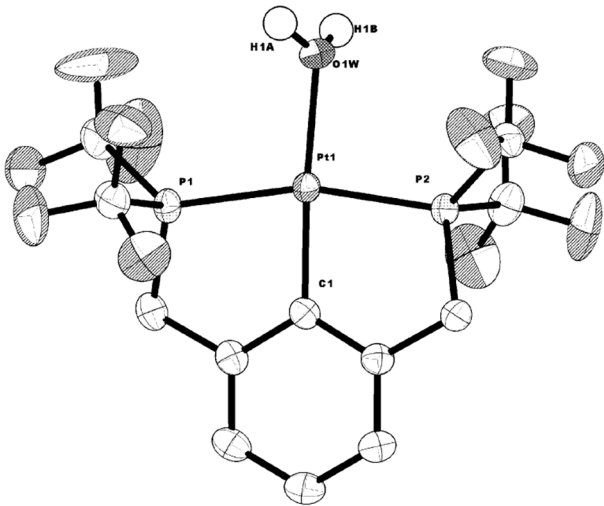
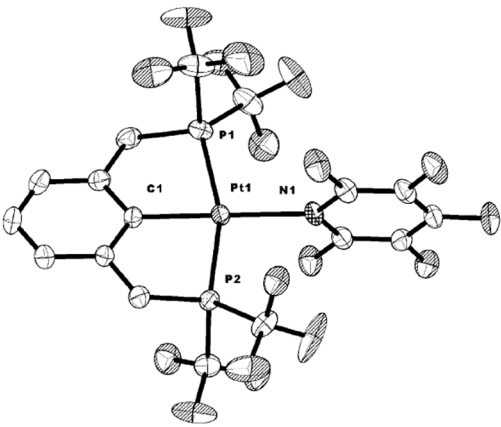
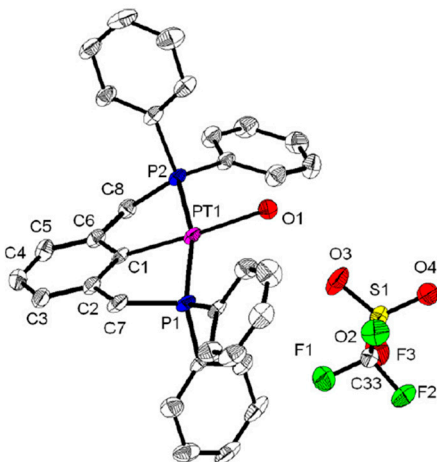


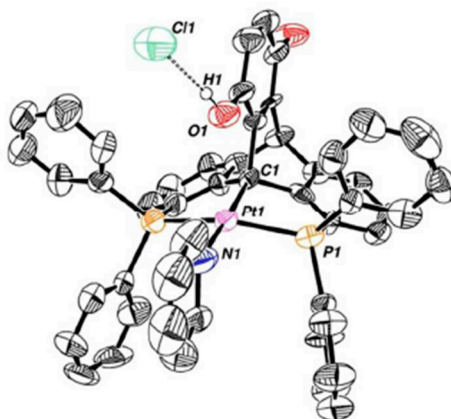
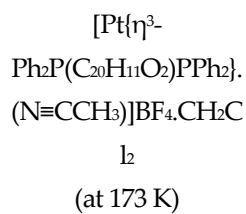
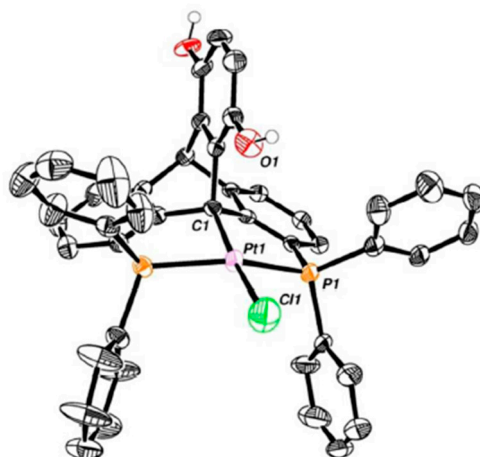
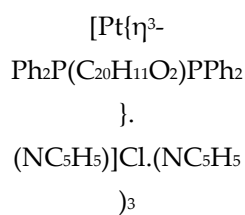
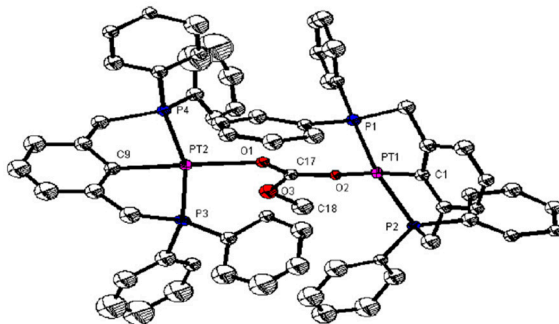
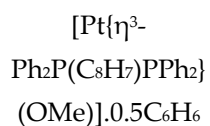
Study of structure and
mechanism of platinum
complex formation; a rare
example of a Pt(0)
complex that adopts a
highly planar coordination
geometry [28]



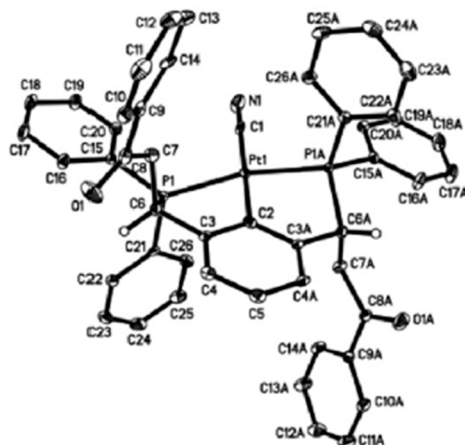
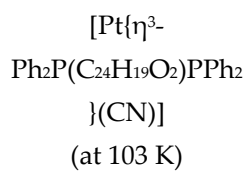
Study of ligand synthesis
and structure of platinum
complex formed; platinum-
catalyzed synthesis of an
unsymmetrical PNP-
pincer-type phosphalkene
ligand (PPEP) from
bis(phosphaethenyl)pyridi
ne (BPEP) via
intramolecular C-H
addition/cyclization of the
CH=PMes* group [29]

Table S2. Structures and applications of $\text{Pt}\{\eta^3\text{-P}^1\text{C}^1\text{P}^2\}(\text{Y})$, ($\text{Y}=\text{O}^2\text{L}, \text{N}^2\text{L}, \text{CL}, \text{Cl}, \text{Br}$) complexes^a

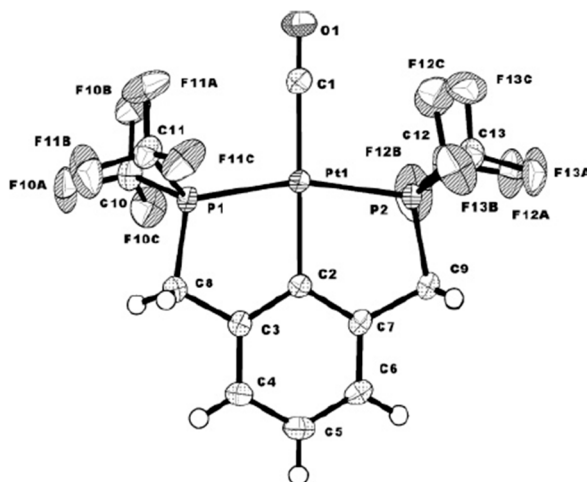
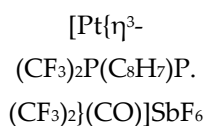
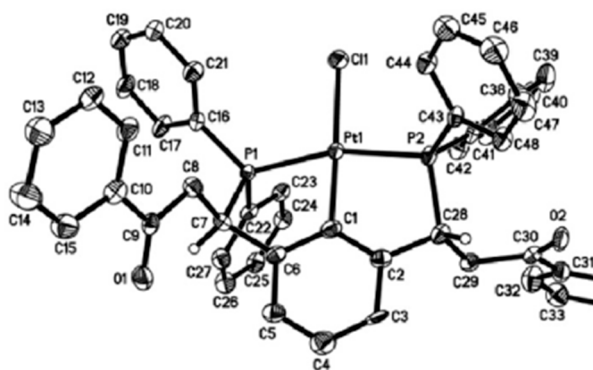
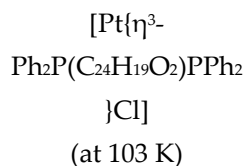
Complex	Structures	Ref.
$[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P(C}_8\text{H}_7\text{)P(CF}_3)_2\}$ $(\text{H}_2\text{O})]\text{SbF}_6$ (at 150 K)		synthetic strategies toward the synthesis of electron-poor pincer complexes serving as a catalyst for ethylene hydrogenation and providing ethylene dimerization activity [30]
$[\text{Pt}\{\eta^3\text{-(CF}_3)_2\text{P(C}_8\text{H}_7\text{)P(CF}_3)_2\}$ $(\text{NC}_5\text{F}_5)]\text{B(C}_6\text{F}_5)_4$ 4 (at 150 K)		
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P(C}_8\text{H}_7\text{)PPh}_2\}$ $(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3$ (at 165 K)		Study on the synthesis, stability and CO ₂ insertion reactivity of a (PCP) platinum methoxide complex [31]



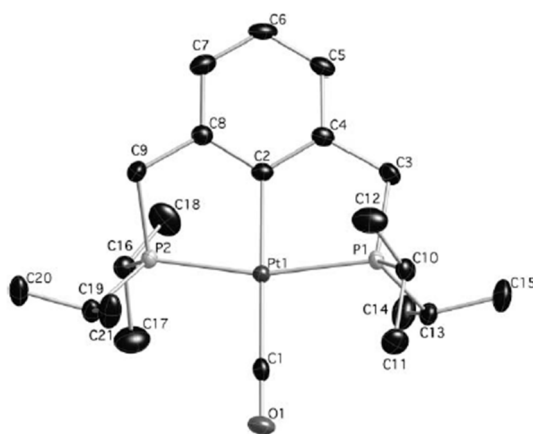
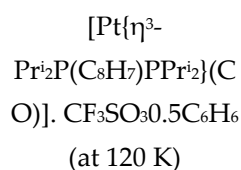
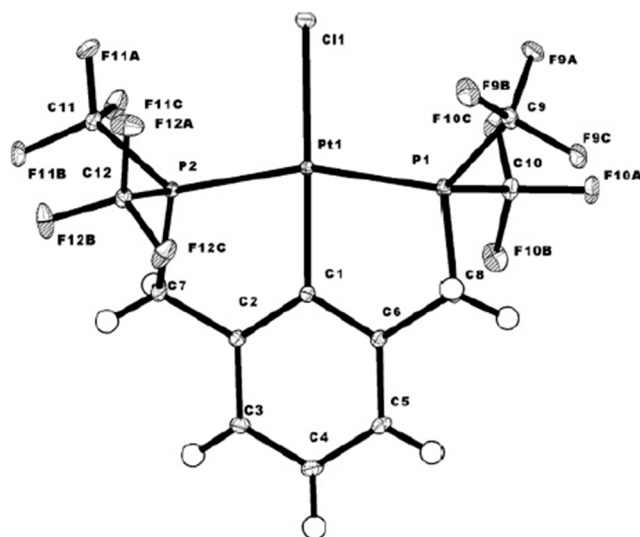
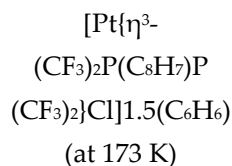
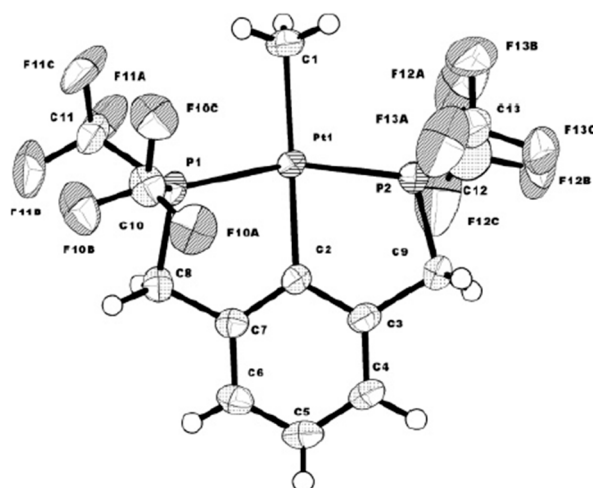
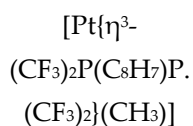
the synthesis,
coordination chemistry
and preliminary
description of the
catalytic properties of
some new platinum
diphosphine $\text{PC}(\text{sp}^3)\text{P}$ -
pincer complexes
bearing
the functionalized
ligand [33]



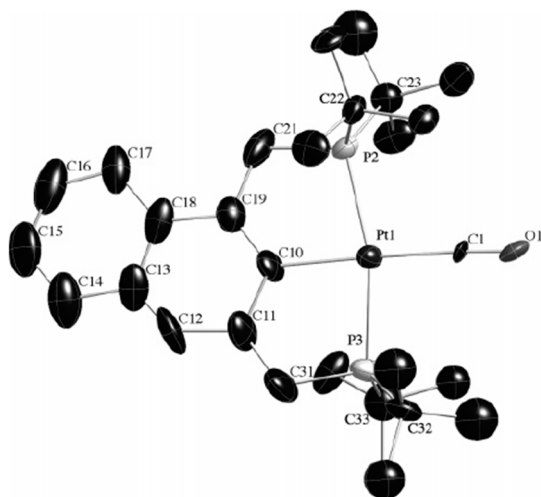
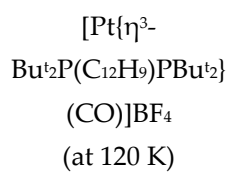
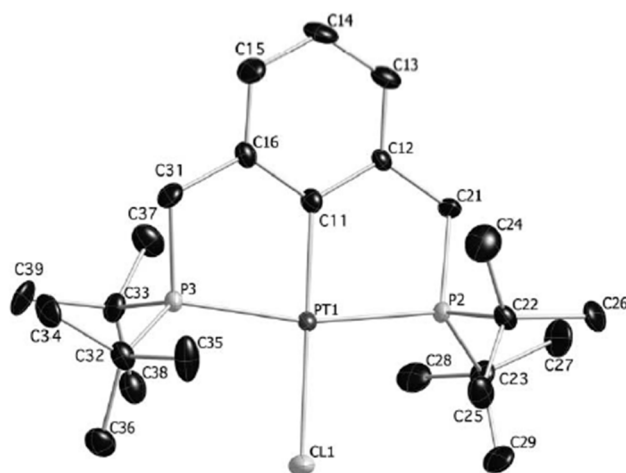
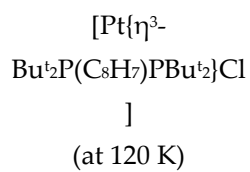
Structural study of Pt–C bonds in P–C–P pincer complexes; pincer complexes as potential (stereo)selective catalysts [34]



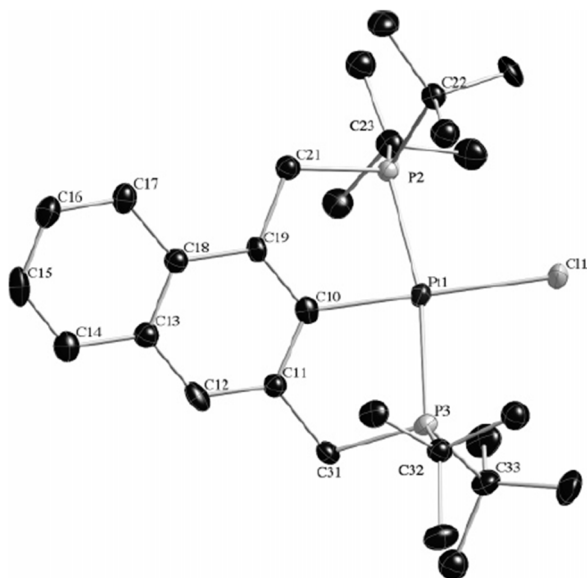
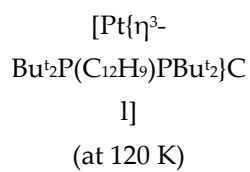
The synthesis of perfluoroalkyl-substituted “pincer”-type PCP ligands, and platinum coordination studies [35]

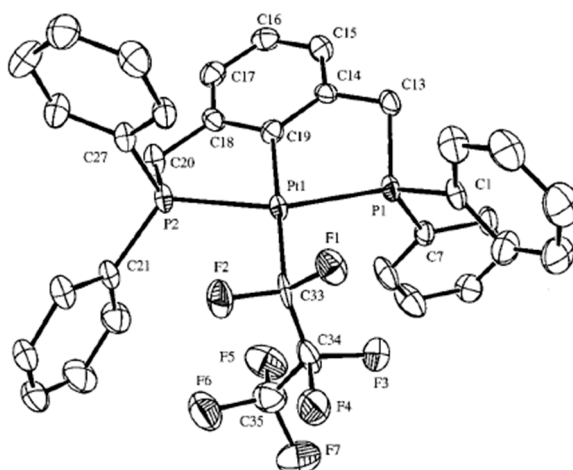
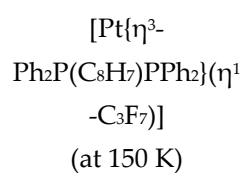


synthesis and characterization of several Pt(II) complexes, including formyl complexes, based on the PCP-type pincer ligands; study on reactivity, stability and the significance of sterics [36]

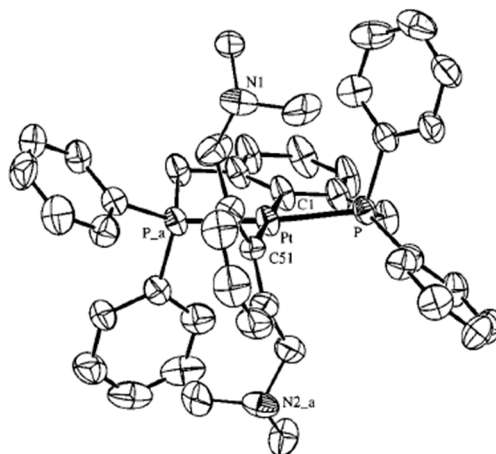
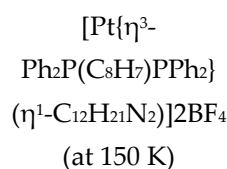


A series of naphthyl-based PCP Pt(II) complexes was synthesized and characterized as for their structure and reactivity; [37]

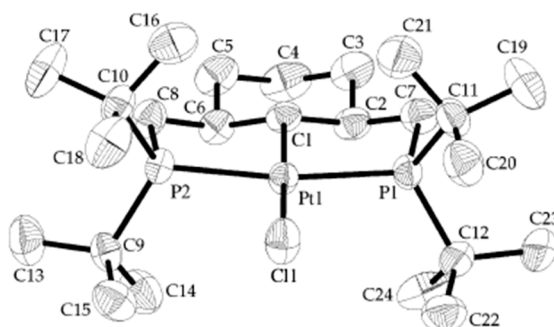
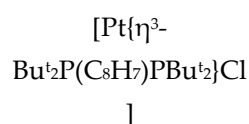




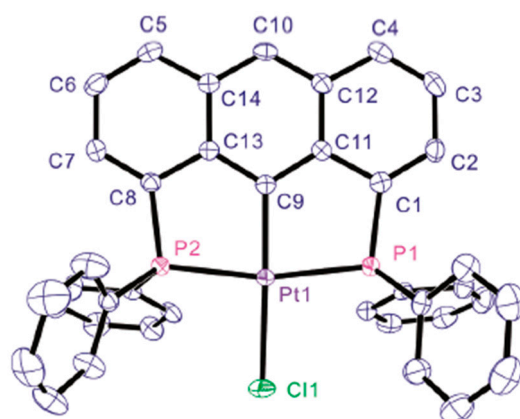
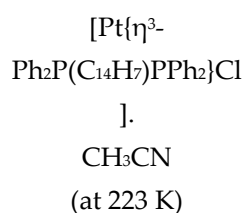
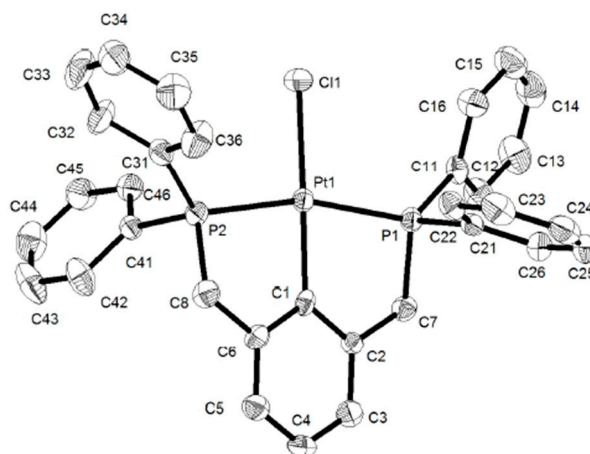
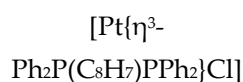
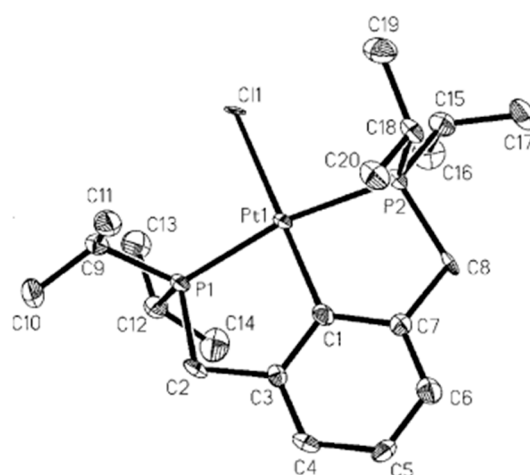
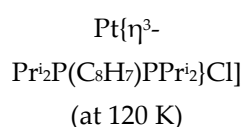
Synthesis and molecular
structure
characterization of a
perfluoroalkyl
complex of platinum
containing a PCP pincer
ligand [38]



The bis(ortho-)chelated
platinum complex has
been used as a novel
metal precursor for C-H
bond activation and
subsequent
cyclometalation of the
potentially
terdentate coordinating
pincer ligand [40]



Extension of the family
of PCP ligands
with aliphatic
cyclohexane backbones;
synthesis and
characterisation of
PCsp³P phosphine and
phosphinite
platinum(II) complexes;
a possible explanation
for the different
reactivity of
phosphine and
phosphinite based
ligands [41]

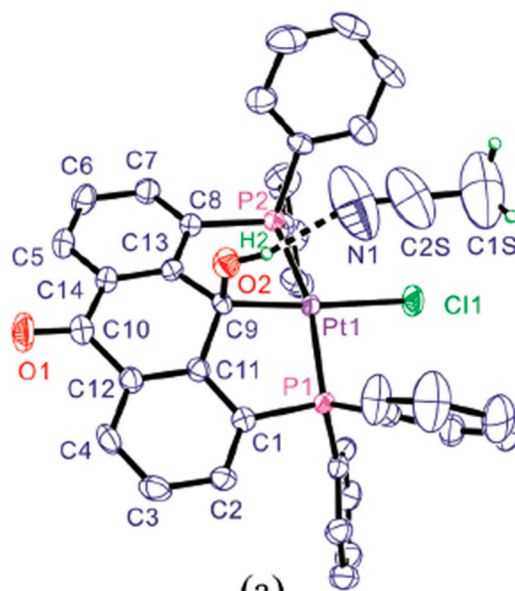


Synthesis and structural characterization of C-metalated diazoalkane complexes of platinum based on PCP- and PCN-type ligands; the reactivity of C-metalated diazoalkane complexes is strongly dependent on the pincer-ligand properties [42]

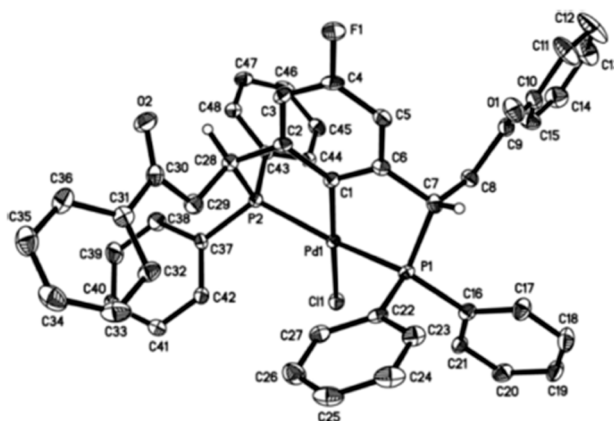
structure report on {2,6-Bis[(diphenylphosphino)methyl]-phenyl}chloroplatinum(II) complex belonging to a group of complexes extensively used in catalysis [43]

Study on photooxidation of a platinum-anthracene pincer complex: formation and structures of PtII-anthrone and -ketal complexes; unlike the photooxidation of anthracene, which gives rise to many of secondary photoproducts and thermal products, photooxygenation of PtII(DPA)Cl (DPA = 1,8-bis(diphenylphosphino)anthracene) produces

[Pt{ η^3 -
Ph₂P(C₁₃H₇O₂)PPh₂}
Cl].CH₃CN
(at 223 K)

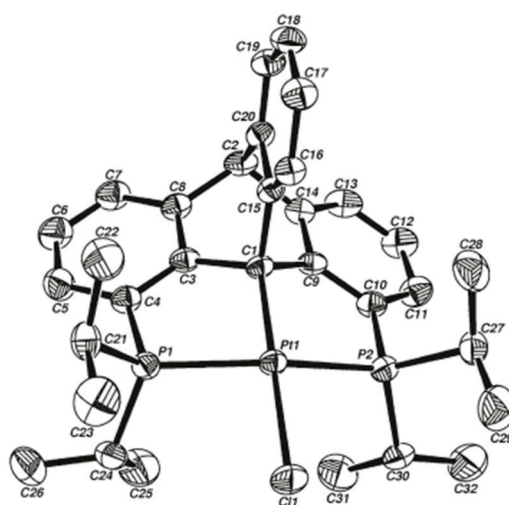
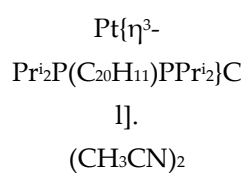


[Pt{ η^3 -
Ph₂P(C₁₈H₁₉O₈)
PPh₂}Cl].CH₂Cl₂
(at 103 K)

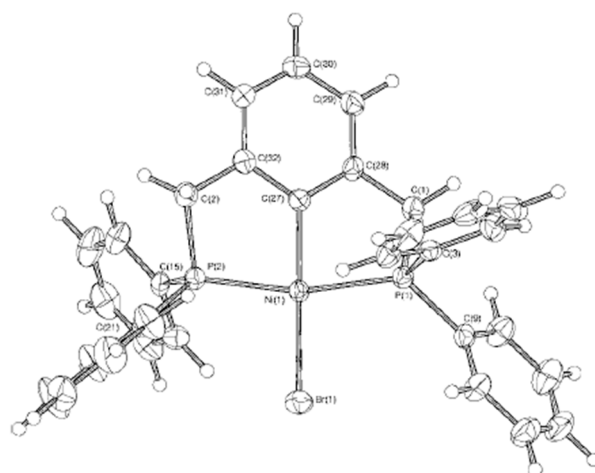
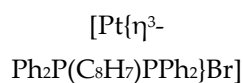


three oxidized
complexes
sequentially [44]

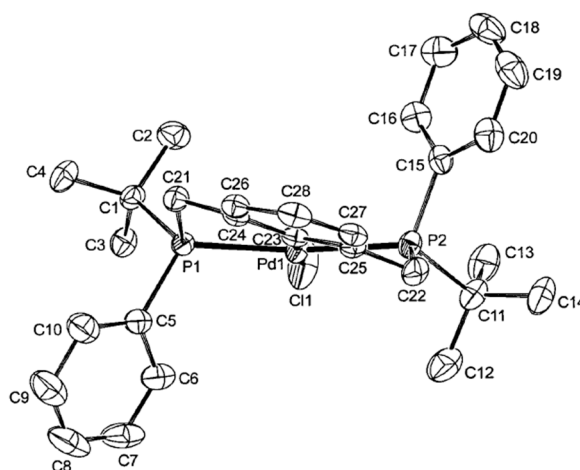
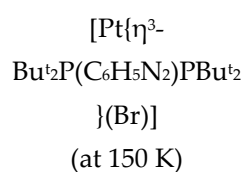
Versatile syntheses and structural characterization of optically pure PCE pincer ligands: facile modifications of the pendant arms and ligand backbones; minor structural changes on these novel pincer complexes affect their chemical properties significantly when they were applied as catalysts for the reaction between diphenylphosphine and chalcone [45]



Trans-chelating bis(diisopropylphosphino)tritycene was employed as a platform for the construction of a new class of C(sp³)-metalated pincer complexes via C-H activation; synthesis and structural study; excellent thermal and conformational stability; unique structural motif for the design of PC(sp³)P-based compounds with new steric and electronic features [46]

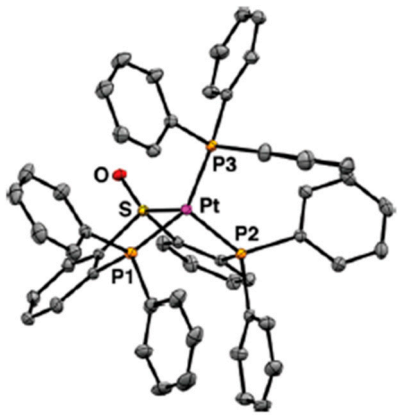
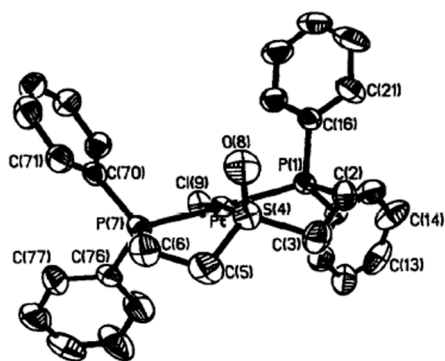
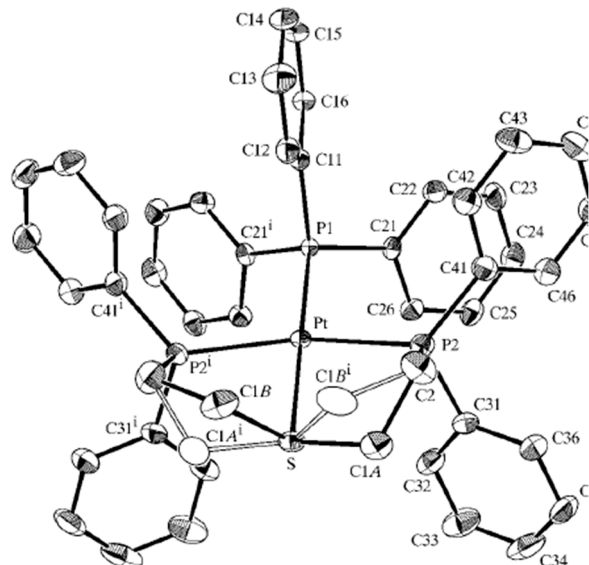


Synthesis and X-ray structural analysis of PtII complex with the potentially tridentate ligand 1,3-bis(diphenylphosphino)methyl)benzene [57]

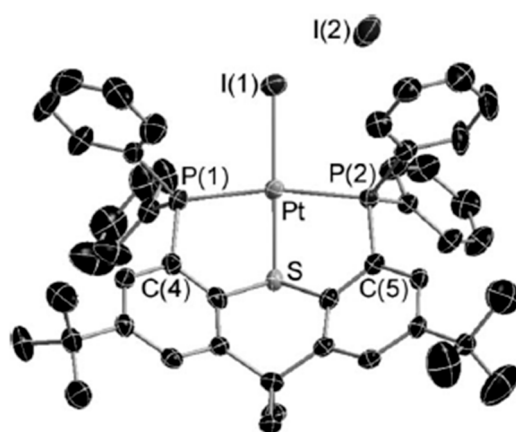


Synthesis and structural characterization of the first P-stereogenic PCP pincer ligands, their metallation by platinum and preliminary catalytic activity study (no significant effect of PtII complexes in chiral catalysis) [47]

Table S3. Structures and applications of $\text{Pt}(\eta^3\text{-P}^1\text{X}^1\text{P}^2)(\text{Y})$, ($\text{X}^1 = \text{S}^1$ or Si^1) ($\text{Y} = \text{C}^2\text{L}, \text{Cl}, \text{P}^3\text{L}, \text{I}, \text{H}, \text{O}^2\text{L}$) complexes^a

Complex	Structures	Ref.
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{S}(=\text{O})(\text{C}_6\text{H}_4)\text{PPh}_2\}(\text{PPh}_3)] \cdot 0.5(\text{CH}_2\text{Cl}_2)$ (at 100 K)		<p>study aimed to assess the electronic effects of incorporating a sulfinyl donor into a pincer-type ligand; the preparation of a new tridentate diphosphinosulfinyl ligand; the synthesis and properties of its (S(O)P2 pincer-type) Pt complexes; the ligand's geometric flexibility and ability to form highly electrophilic complexes may prove useful for bond activation processes and catalysis [48]</p>
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{S}(=\text{O})(\text{CH}_2)_2\text{PPh}_2\}(\text{Cl})] \cdot \text{ClO}_4$		<p>synthesis and structural analysis of square-planar platinum(II) complex with a novel P-S(O)-P tridentate ligand as a potential stable chiral catalyst [49]</p>
$[\text{Pt}\{\eta^3\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2\}(\text{PPh}_3)] \cdot 2\text{ClO}_4 \cdot \text{Me}_2\text{CO}$ (at 120 K)		<p>investigation of the relationship between structure and reactivity of tridentately chelated Pt(II) complexes; synthesis and structural characterization of [bis(2-diphenylphosphinoethyl)sulfide-κ3P,S,P'](triphenylphosphine-κP)platinum(II) diperchlorate acetone solvate [50]</p>

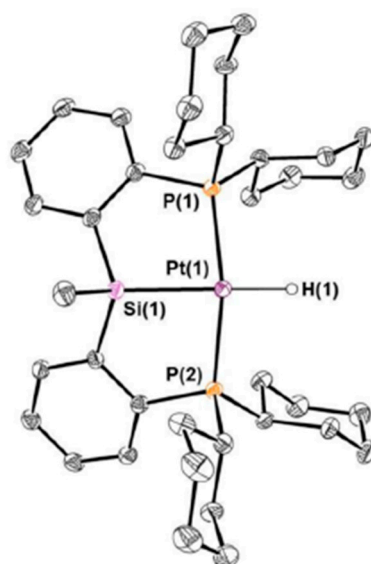
[Pt(η^3 -
Ph₂P(C₂₃H₂₈S)PPh₂)
(I)](I).1.74 CH₂Cl₂
(at 173 K)

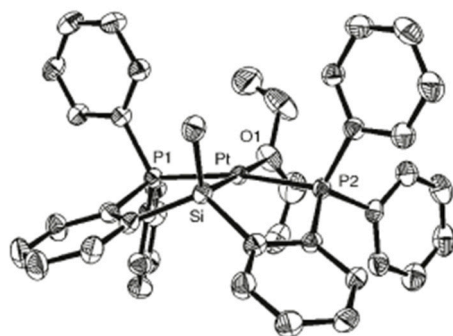
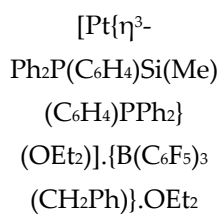


Pt(II) complexes of an ambiphilic PSB-ligand: investigations into η^3 (BCC)-triarylborane coordination (synthesis and structural characterization); besides fundamental studies into the electronic consequences and metal-ligand interactions involved in metal-borane coordination, metal-borane complexes are also of great interest for the development of new catalytic reactivity (increase of the coordination number by one, reduction of the d-electron count by two units, often resulting in unusual geometries for a given d-electron configuration, binding, positioning and/or activating organic substrates (bifunctional catalysis), coordination or abstraction) [51]

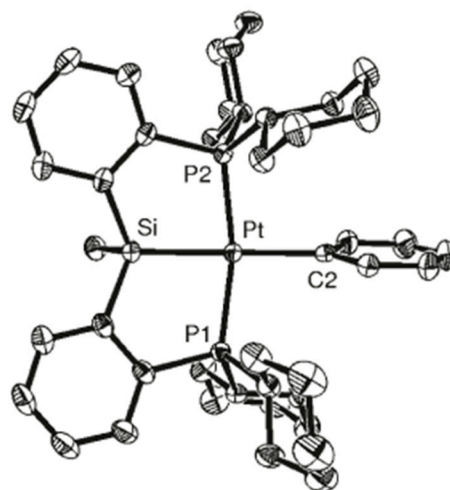
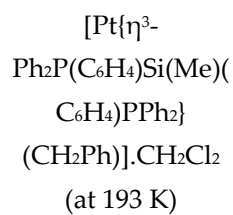
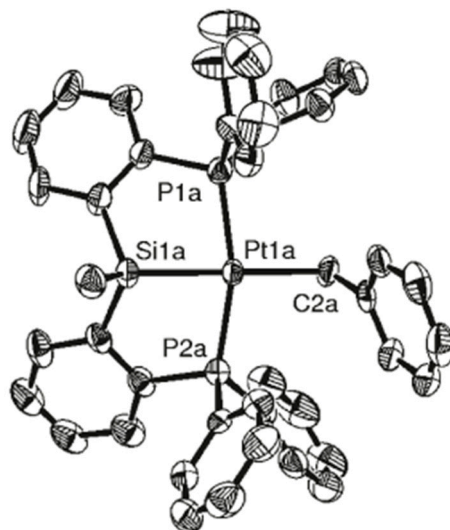
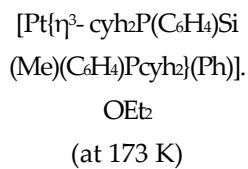
structural study on characterization the solution and solid-state structures of Pt PSiP pincer-supported hydrides [52]

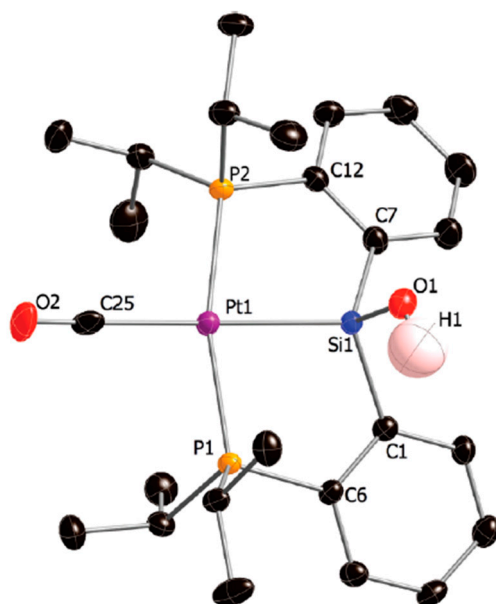
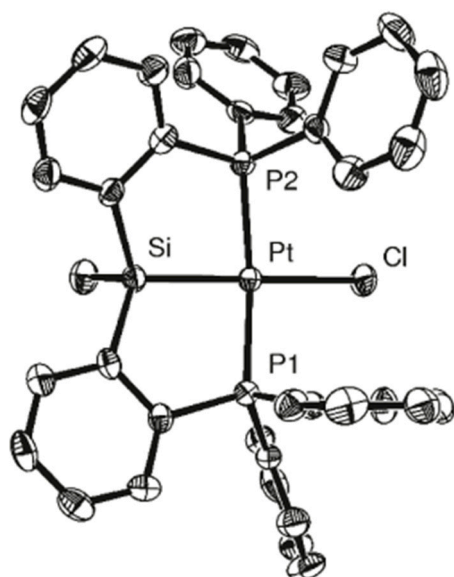
[Pt(η^3 -
cyh₂P(C₆H₄)Si(Me).
(C₆H₄)Pcyh₂}(H))].0.
5 pentane (at 150 K)



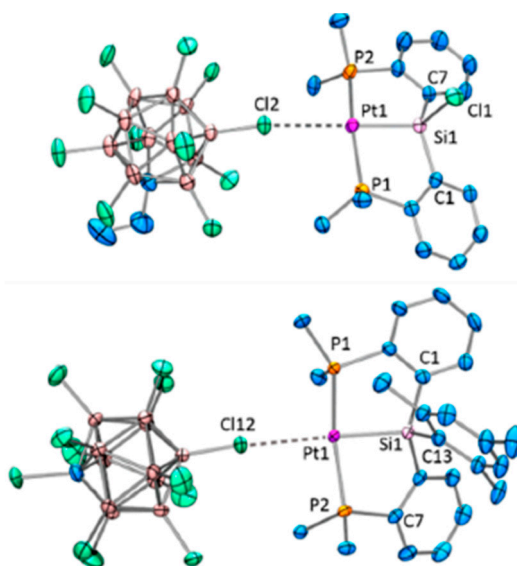
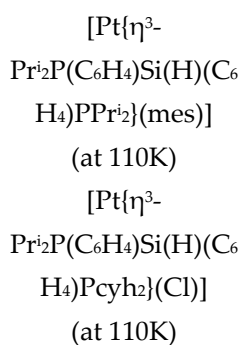
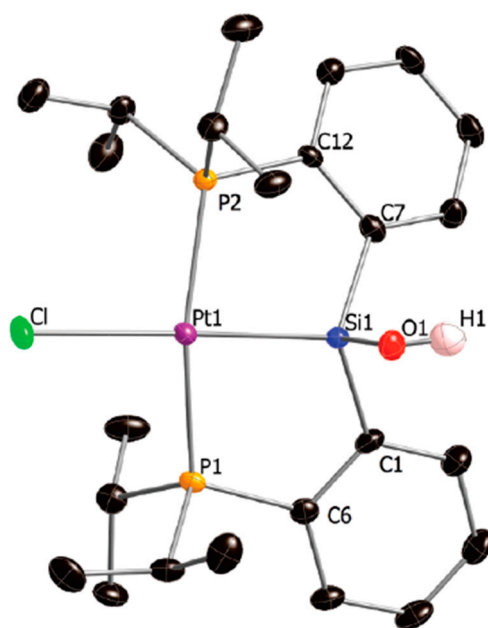
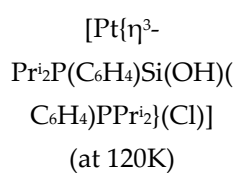


synthesis and characterization of a new series of neutral and cationic platinum(II) complexes bearing the tridentate pincer-like bis(phosphino)silyl ligands: Si-H and Si-Cl bond activation chemistry (modification of the steric and electronic properties of the [R-PSiP] ligand directs the outcome of reactions with hydrido-chlorosilanes toward either Si-H or net Si-Cl bond cleavage) [53]

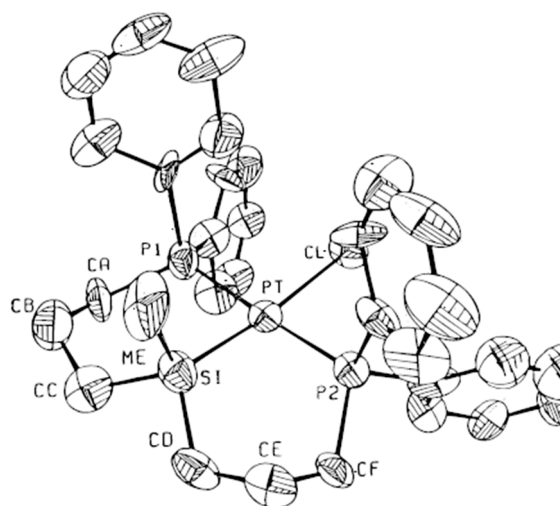
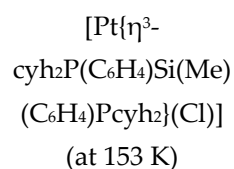




synthesis, structure, and unusual reactivity of silanol-based pincer Pt(II) complexes; dual reactivity, hydrolytic rearrangement and coupling resulting in the unusual mono- or binuclear complexes [54]



Silyl–silylene interplay in cationic PSiP pincer complexes of platinum; species of the type $(\text{P}_2\text{Si}=\text{PtR})$ undergo a net 1,2-migration of R from Pt to Si, which leads to highly unsaturated Pt cations displaying only a very distant interaction with the weakly coordinating carborane anion; synthesis and structural study [55]



Study on the stereochemistry of the tridentate bis(diphenylphosphinopropyl)silyl (biPSi) framework; complexation providing discrimination at coordinatively unsaturated metal centers; synthesis and structural characterization of $\text{Pt}[\text{SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ complex [56]