*Inorganics* **2015**, *3*, 118-138; doi:10.3390/inorganics3020118

OPEN ACCESS

*inorganics*

**ISSN 2304-6740**

www.mdpi.com/journal/inorganics

*Article*

# Five Coordinate Platinum(II) in [Pt(bpy)(cod)(Me)][SbF$_6$]: A Structural and Spectroscopic Study

**Axel Klein [1,*], Michael Neugebauer [1], Alexander Krest [1], Anna Lüning [1], Simon Garbe [1], Natalia Arefyeva [1] and Nils Schlörer [2]**

[1] Institut für Anorganische Chemie, Department für Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany; E-Mails: michael.neugebauer@web.de (M.N.); alexander@krest.de (A.K.); a.luening@gmail.com (A.L.); s.garbe@uni-koeln.de (S.G.); arefyeva@aol.com (N.A.)

[2] NMR platform, Department of Chemistry, University of Cologne, Greinstrasse 4, D-50939 Cologne, Germany; E-Mail: nils.schloerer@uni-koeln.de

* Author to whom correspondence should be addressed; E-Mail: axel.klein@uni-koeln.de;
Tel.: +49-221-470-4006; Fax: +49-221-470-4899.

Academic Editor: Elena Lalinde

*Received: 7 April 2015 / Accepted: 5 May 2015 / Published: 13 May 2015*

**Abstract:** The five coordinate organoplatinum complex [Pt(bpy)(cod)(Me)][SbF$_6$] (cod = 1,5-cyclooctadiene, bpy = 2,2'-bipyridine) was obtained reacting [Pt(cod)(Me)Cl] with Ag[SbF$_6$] and bpy and characterized by multiple spectroscopy (IR and NMR) and single crystal XRD. Although the application of the $\tau$ values for the discrimination between trigonal bipyramidal *vs.* square pyramidal coordination fails, the molecular structure can be unequivocally described as basally-distorted trigonal bipyramidal. Detailed multinuclear NMR spectroscopy in solution at ambient temperature gives strong evidence for the same structure; corresponding low-temperature measurements down to −70 °C revealed no marked dynamic processes.

**Keywords:** organoplatinum; five coordinate Pt(II); diolefin ligands; diimine ligands; multi-nuclear NMR; XRD

## 1. Introduction

From general considerations, five coordinate Pt(II) complexes are a bit unusual. Due to its $d^8$ configuration and a very strong ligand field (5d element), platinum in the oxidation state +2 has a strong tendency to form square planar coordinated $[PtL_4]^n$ ($n$ = charge) complexes. The non-occupation of the high-energy $dx^2$-$y^2$ orbital and the stabilization of the $dz^2$ orbital are energetically the main reasons for this [1]. The highest occupied metal orbital is thus dxy, and this is considered to be the reason that binding to further ligands in the axial positions is not favored. However, this only rules out stable five coordinate Pt(II) complexes with a square-pyramidal configuration. Thus, it is generally assumed that five coordinate Pt(II) complexes with a trigonal bipyramidal geometry might be stable or intermediate species, while square pyramidal species rather have the character of a transition state [2–4]. Indeed, most of the structurally-characterized five coordinate Pt(II) complexes exhibit clearly a trigonal bipyramidal geometry [4–20]. Interest in five coordinate Pt(II) species and their Pd(II) analogues comes from their involvement as intermediates in important Pt(II) or Pd(II) catalyzed organometallic transformations [3,21–28].

Quite frequently, such pentacoordination is reported for Pt(II) or Pd(II) complexes with olefin ligands, and here, the catalytic relevance is obvious. In one of the most important transition metal catalyzed processes, the oxidation of ethylene, better known as the Wacker Hoechst process (also Wacker oxidation) [29–32], the crucial step is the nucleophilic attack of $OH^-$ or $OH_2$ to the bound ethylene in $[Pd(C_2H_4)Cl_3]^-$, which is the Pd derivative of the complex anion in $K[Pt(C_2H_4)Cl_3]$, Zeise's salt, probably the oldest organoplatinum compound [33–41]. For the Wacker system $[Pd(C_2H_4)Cl_3]^-$, two different mechanisms were assumed for this hydropalladation reaction, an intramolecular addition of the OH ligand in *cis*-$[Pd(C_2H_4)(OH)Cl_2]$ (*syn*-addition) or an external attack of $H_2O$ (*anti*-addition) to the bound olefin [29,31]. For the *syn*-addition mechanism, a five coordinate transition state $\{[Pd(\eta^3\text{-}O,\alpha H,C\text{–}HO\text{–}CH_2CH_2)Cl_2]\}^{\neq}$ with an agostic C–H···Pd bond was calculated [29,31]. For the Zeise anion $[Pt(C_2H_4)Cl_3]^-$, analogous reactions have been studied [42–44] and the Zeise anion or its dimer $[(C_2H_4)ClPt(\mu\text{-}Cl_2)PtCl(C_2H_4)]$ have been used as catalysts in many more important transformations, such as hydroaminations, hydrosilylations or alkoxyarylations [29,45–47]. In the presence of chelate nitrogen ligands, such as diimines (N^N), five coordinate species were discussed in such catalytic processes [42,43,48–52].

Indeed, when reacting the Zeise anion with diimine ligands (N^N), five coordinate complexes $[Pt(N\text{^}N)(\eta^2\text{-}C_2H_4)Cl_2]$ were obtained [48–60]. The mono-olefin complexes of the type $[Pt(N\text{^}N)(\eta^2\text{-olefin})X_2]$ (X = halogens and pseudohalogens) form indeed the main body of the so far reported organometallic pentacoordinate Pt(II) complexes [4,5–20,48–71].

In contrast to this, diolefin ligands in five coordinate Pt(II) complexes were scarce. Previously, it had been reported that the reaction of the diolefin complex [Pt(cod)Cl(Me)] (cod = 1,5-cyclooctadiene) with diimine ligands N^N in the presence of Cl-abstracting agents, such as $NaBF_4$ or $AgBF_4$, leads to five coordinate cationic $[Pt(N\text{^}N)(cod)(Me)]^+$ (N^N = various pyridine-2-carbaldimines) complexes [72]. One of them, $[Pt(L)(cod)(Me)](BF_4)$ with L = *N*-((6-chloropyridine-2-yl)methylene)-4-methoxyaniline) has been structurally characterized [72]. The crystal and molecular structure of a palladium derivative $[Pd(Rphen)(cod)(Me)]^+$ (Rphen = 2,9-(4-*t*Bu-$C_6H_4$)-1,10-phenanthroline), carrying a quite bulky 1,10-phenanthroline as a diimine ligand, has also been reported [73]. Earlier reports postulated quite similar species $[M(N^\wedge N)(cod)Cl]^+$ (M = Pt or Pd) as intermediates during reactions of $[M(diene)Cl_2]$ complexes with N^N ligands in the presence of nucleophiles (Nu), finally forming complexes $[M(en\text{-}yl)(N^\wedge N)]^+$ in which a nucleophile has been added to one of the diene double bonds, creating a M–C–Nu sigma bond [74–79]. Reaction of the four coordinate cod complex [Pt(cod)(Ph)(L)] carrying the hemilabile amino-carboxylate ligand *ce*-$ArCH_2NH_2CH_2C_6H_4COO^-$ (*ce* = crown ether) with 2,2'-bipyridine (bpy) produces the structurally-characterized five coordinate complex $[Pt(bpy)(cod)(Ph)]^+$ [80]. Further reported five coordinate Pt(II) complexes with diene or polyene ligands were the complexes $(PPN)_2[Pt(SnCl_3)_3L]$ (PPN = bistriphenylphosphiniminium; L = 1,5-cyclooctadiene (cod) or 2,5-norbornadiene (nbd)) [81], the complex $[(DMBN)(C_2H_4)PtCl_2]$ (DMBN = 3,7-dimethylenebicyclo[3.3.l]nonane), which contains a diene and ethene at the same time [82], the tris-ene complex $[(P)PtCl]^+$ (P = tri(1-cyclohepta-2,4,6-trienyl)phosphine) [83] and the cod-bridged binuclear complex $[(\mu\text{-}cod)\{Pt(Me)(R_2Bpz_2)\}_2]$ ($R_2Bpz_2$ = diorganobis(l-pyrazolyl) borate) [84], a binding mode that has also been assumed for the above-mentioned reactions of $[Pt(N^\wedge N)Cl_2]$ with dienes [74]. Furthermore, five coordinate intermediates $[Pt(dien)L(tu)]^{2+}$ (dien = diethylenetriamine; tu = thiourea; L = Ado-N7 (adenosine) or Guo-N7 (guanosine)) have been proposed from stereochemical and kinetic observations [85,86].

The pentacoordinate title complex $[Pt(bpy)(cod)(Me)][SbF_6]$ was obtained when trying to synthesize the binuclear organometallic platinum(II) complex $[(\mu\text{-}bpy)\{Pt(bpy)(Me)\}_2]^{2+}$, containing bpy as the chelate and bridging ligand at the same time. The corresponding Pd complexes $[(\mu\text{-}\eta^1,\eta^1\text{-}N^\wedge N)\{Pd(N^\wedge N)(Me)\}_2][SbF_6]_2$ containing either 2,2'-bipyridine (bpy) or 4,4'-dimethyl-2,2'-bipyridine (dmbpy) were recently reported by us [26,87]. In this contribution, we will report on the NMR spectroscopy in solution and the crystal and molecular structure of $[Pt(bpy)(cod)(Me)][SbF_6]$ in the solid and will compare the data to related five coordinate Pt(II) complexes.

## 2. Results and Discussion

### 2.1. Preparations and Analytical Characterization

Initial reactions were carried out dedicated to synthesizing the binuclear organometallic platinum(II) complex $[(\mu\text{-}bpy)\{Pt(bpy)(Me)\}_2]^{2+}$ containing bpy as the chelate and bridging ligand, using a procedure that was successfully applied recently for the Pd derivatives $[(\mu\text{-}\eta^1,\eta^1\text{-}N^\wedge N)\{Pd(N^\wedge N)(Me)\}_2][SbF_6]_2$ (N^N = 2,2'-bipyridine (bpy) or 4,4'-dimethyl-2,2'-bipyridine (dmbpy)) [87]. To this end, we used a 2:2:1 ratio of [Pt(cod)(Me)Cl], $Ag[SbF_6]$ and bpy in (non-dried) acetone solution. However, instead of the binuclear complex $[(\mu\text{-}bpy)\{Pt(bpy)(Me)\}_2]^{2+}$, we observed mixtures of the title complex $[Pt(bpy)(cod)(Me)]^+$ and the aqua complex $[Pt(cod)(Me)(H_2O)]^+$ in approximately 1:1 ratios. From these mixtures, the aqua complex was characterized unequivocally by NMR (see the Experimental Section). When using equimolar amounts (1:1:1) of [Pt(cod)(Me)Cl], $Ag[SbF_6]$ and bpy, the title complex $[Pt(bpy)(cod)(Me)][SbF_6]$ was obtained in pure form and in good yields (for details, see the Experimental Section).

The reason why the Pt derivative of the recently reported binuclear Pd complex [(μ-bpy){Pd(bpy)(Me)}$_2$][SbF$_6$]$_2$ [87] could not be observed at all under the chosen reaction conditions lies very probably in the far slower kinetics of Pt(II) compared with Pd(II).

### *2.2. Crystal and Molecular Structures*

From a saturated acetone solution, single crystals of [Pt(bpy)(cod)(Me)][SbF$_6$] were obtained. The structure was solved and refined in the monoclinic space group $P2_1/c$ with the results depicted in Figure 1 (data in Table 1).

**Table 1.** Details of the crystal structure determination and selected structural data of [Pt(bpy)(cod)(Me)][SbF$_6$].

| | |
|---|---|
| Formula/weight (g/mol) | $C_{19}H_{23}F_6N_2Pt_1Sb_1$/710.23 |
| crystal system/space group | monoclinic/$P2_1/c$ |
| cell $a/b/c$ (Å)/β (°) | 11.8078(9)/8.3564(7)/21.0767(18)/99.052(6) |
| $V$ (Å)$^3$/$Z$ | 2053.8(3)/4 |
| $\rho_{calc}$ (g/cm$^3$)/μ (mm$^{-1}$) | 2.297/8.180 |
| Limiting indices | $-15 < h < 13$; $-10 < k < 10$ ; $-26 < l < 26$ |
| Refl. coll./uniq./$R_{int}$ | 24,259/4504/0.1210 |
| data/restraints/param. | 4504/0/264 |
| goof. on $F^2$ | 1.163 |
| final $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0644/0.1613 |
| $R_1$, $wR_2$ (all data) | 0.0675/0.1629 |
| $\Delta\rho_{min/max}$ ($10^{-6}$ e/pm$^3$) | –3.242/4.279 |
| distances (Å) | |
| Pt–N10,N20 | 2.225(9), 2.222(9) |
| Pt–C41 | 2.090(11) |
| Pt–C35,C36 | 2.105(10), 2.093(10) |
| Pt–C31,C32 | 2.295(12), 2.339(12) |
| Pt–$X_1$, Pt–$X_2$ [a] | 1.962(10), 2.215(10) |
| C31–C32, C35–C36 | 1.360(18), 1.495(18) |
| C11–C21 | 1.482(16) |
| angles (°) | |
| N10–Pt–N20 | 72.8(3) |
| $X_1$–Pt–$X_2$ | 85.5(1)° |
| N10–Pt–C41, N20–Pt–C41 | 86.6(4), 85.3(4) |
| C41–Pt–$X_1$, C41-Pt–$X_2$ | 89.9(3)°, 175.4 (3)° |
| N10–Pt–$X_1$, N10–Pt–$X_2$ | 143.7(2)°, 97.5(2)° |
| N20–Pt–$X_1$, N20–Pt–$X_2$ | 142.9(3)°, 97.9(3)° |
| Sum of angles around Pt [b] | 359.4(2) |

[a] $X_1$ = centroid of the equatorial C35–C36 bond; $X_2$ = centroid of the axial C31–C32 bond. [b] As defined by N10, N20 and $X_1$.

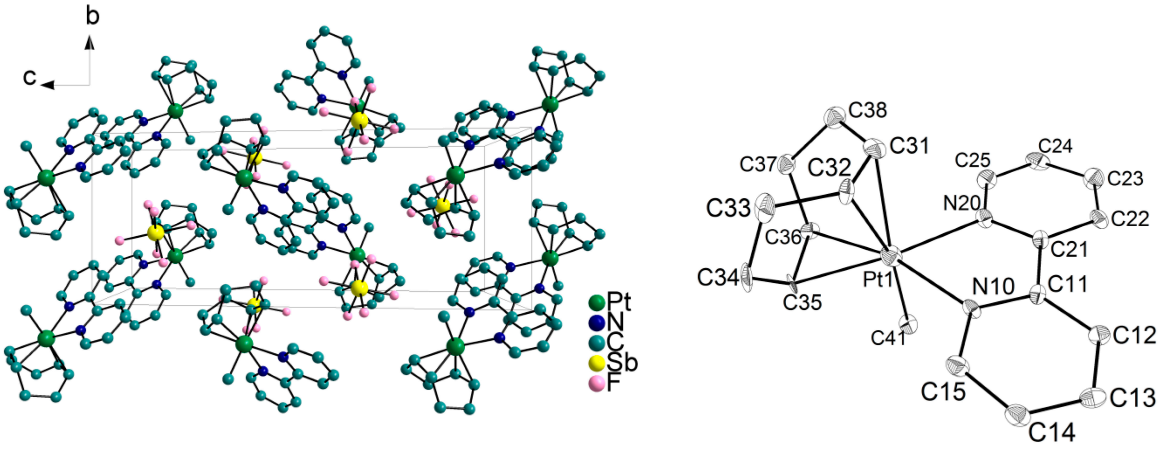
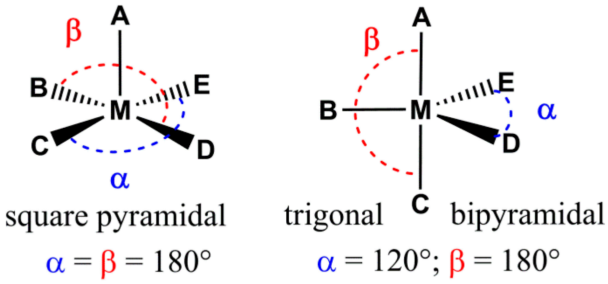


**Figure 1.** Crystal structure of [Pt(bpy)(cod)(Me)][$SbF_6$] (bpy = 2,2'-bipyridine, cod = 1,5-cyclooctadiene) (**left**; viewed along the crystallographic *a* axis) and the molecular structure of the complex cation (**right**; at 50% probability level (with numbering); protons were omitted for clarity).

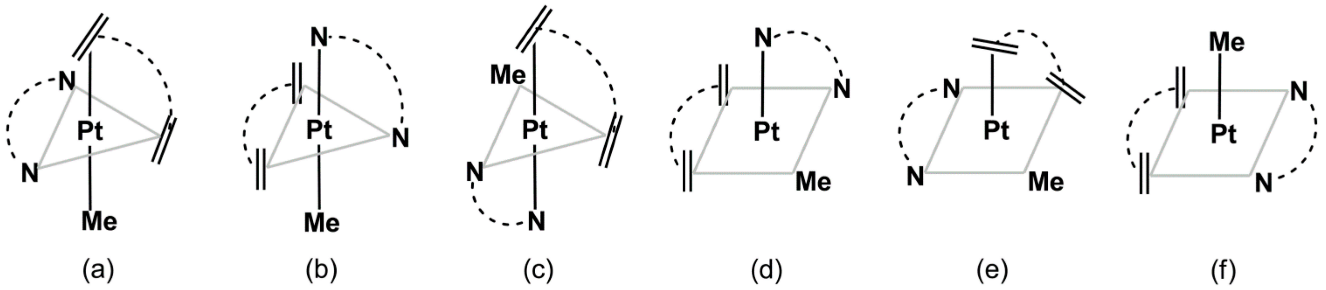
A number of weak intermolecular contacts were observed; amongst them are rather weak H···F hydrogen bridges (shortest H···F distance of 2.407(10) Å and the graphite-type π-π-stacking of the bpy ligands (interplanar distance of 3.8015(3) Å). They both contribute probably only weakly to the crystal structure and have no impact on the molecular structure (for detailed information, see the Figures and Tables in the Supplementary Material).

The molecular structure shows a five coordinate complex with both the bpy and the cod ligand in chelate binding. A closer look reveals that one of the olefin groups shows a tighter bonding to Pt with a Pt–X (X = centroid of the olefin bond) of 1.962(10) Å ($X_1$), while the other reveals a distance of 2.215(10) Å ($X_2$). The same huge differences were found for the much related complex [Pt(N^N')(cod)(Me)]($BF_4$) with N^N' = *N*-((6-chloropyridine-2-yl)methylene)-4-methoxyaniline) [72]. The overall geometry for five coordinate complexes can be drawn from the so-called *tau*-value $\tau = (\beta - \alpha)/60$ [88,89] with α and β being the largest basal angles. τ is one for an ideal trigonal bipyramid and zero for a square-pyramidal coordination (Scheme 1).



**Scheme 1.** The square pyramidal and trigonal bipyramidal geometries with the basal angles α and β. Note that α = β is 180° for the square pyramid only in case that the metal atom lies within the basal plane.

For the title complex, $\tau = 0.528$, which appears to be lying in-between the two geometries. However, the $\alpha$ angle is enlarged due to the rather small chelate bite angle of the bpy ligand of 72.8(3)° found in the trigonal plane of the trigonal bipyramidal coordination. Interestingly, the bpy bite angle of the title complex is somewhat smaller compared with reported values for square planar bpyPt complexes, all lying around 80° [90–93]. Furthermore, the $\beta$ angle might be decreased by the chelate bite angle of the cod ligand. The angle of 85.5° found for the title complex is quite normal for codPt complexes [94–96]. The even smaller $\tau$ values of 0.48 and 0.47 reported for the two independent molecules of $[\mathrm{Pt(N^{\wedge}N')(cod)(Me)}](\mathrm{BF_4})$ [72] and the $\tau = 0.5$ for $[\mathrm{Pd(phen)(cod)(Me)}]^+$ [73] were also governed by these restraints, as were the parameters of related five coordinate Ir or Rh complexes [73]. Thus, for five coordinate complexes of this type with chelate ligands, the $\tau$ value seems to fail to allow an unequivocal geometrical description. Nevertheless, the almost linear Me–Pt–X$_2$ angle (175.4(3)° and the two almost equal X$_1$–Pt–N angles of about 143° justify a description of the title complex as a basally-distorted trigonal bipyramid, as depicted as Structure (a) in Scheme 2. This is supported by the very long Pt–X$_2$ bond of 2.215(10) Å, which can be explained from the position of X$_2$ *trans* to the strong Me coligand (Pt–Me: 2.090(11) Å). In related square planar codPt complexes, the Pt–X distances correlate roughly with the strength of the *trans*-oriented ligand [44,94–104]. For [Pt(cod)(Me)Cl], the Pt–X distance is 1.980(1) Å for the centroid *trans* to the weak Cl coligand and 2.160(1) Å for the Pt–X bond *trans* to the Me coligand, respectively. Thus, the Pt–X$_2$ bond length in the title complex largely exceeds the values found for square planar codPt complexes [44,94–104]. No ligand *trans* to X$_2$ should however lead to a short X$_2$–Pt bond. Thus, Structure (e) from Scheme 2 can be ruled out from the long Pt–X$_2$ bond, and Structures (b), (d) and (f) can be ruled out from the two very different Pt–X bonds. For a description of the complex as in Structure (c), the X$_2$–Pt–Me angle is far too large, and the relatively long Pt–Me bond points to a *trans*-oriented X$_2$ ligand, as in Structure (a); in square planar codPt(Me) complexes, the Pt–Me bond lengths range from 2.05 to 2.1 Å [94–96,101–103]. No ligand *trans* to Me as in Structure (c) would probably lead to a rather small Pt–Me distance. The various *trans* influences of the ligands will be further substantiated in the NMR section below.



**Scheme 2.** Possible geometries for five coordinate $[\mathrm{Pt(bpy)(cod)(Me)}]^+$.

A very similar trigonal bipyramidal structure with an axial methyl coligand *trans* to one of the olefin groups of cod has been recently postulated in the reaction of [Pd(cod)(Me)Cl] with Ag[SbF$_6$] and Me$_2$-Xyl-DAB (Me$_2$-Xyl-DAB = 2,3-dimethyl-1,4-bis(2,6-dimethylphenyl)-diazabuta-1,3-diene). This intermediate is thought to undergo a Me-to-Pd-olefin bond migratory insertion, leading to a cyclometalated product, which undergoes further re-arrangement reactions to finally form a $\eta^3$-allyl complex [(Me$_2$-Xyl-DAB)Pd($\eta^3$-6-methyloct-2-en-1-id)][SbF$_6$] with a 6-Me-cyclooct-2-en-1-id coligand [87].

### *2.3. NMR Spectroscopy*

The title complex [Pt(bpy)(cod)(Me)]$^+$ was studied in detail by multinuclear NMR spectroscopy, as shown in Figures 2–4, allowing the complete assignment of all C and H atoms (Scheme 3).

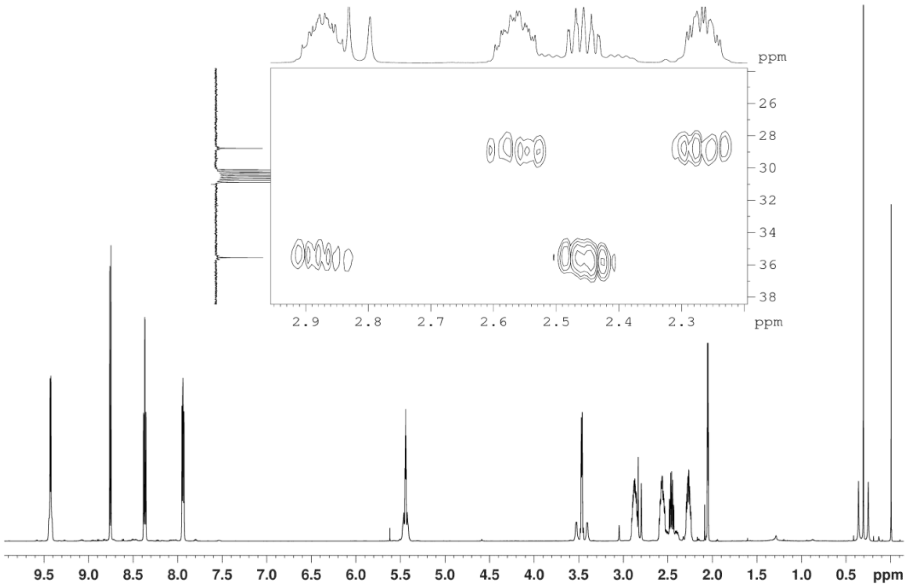


**Figure 2.** The 600 MHz $^1$H NMR spectrum of [Pt(bpy)(cod)(Me)][SbF$_6$] in acetone-d$^6$. Insert on top: section of the $^1$H-$^{13}$C HMQC spectrum at 600 MHz showing the four signals for the cod –CH$_2$– groups (at 298 K).

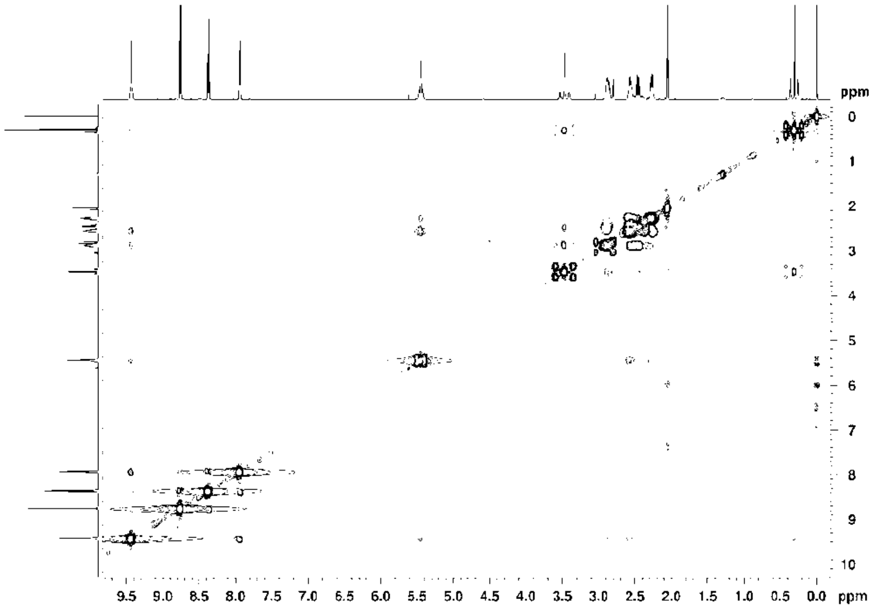
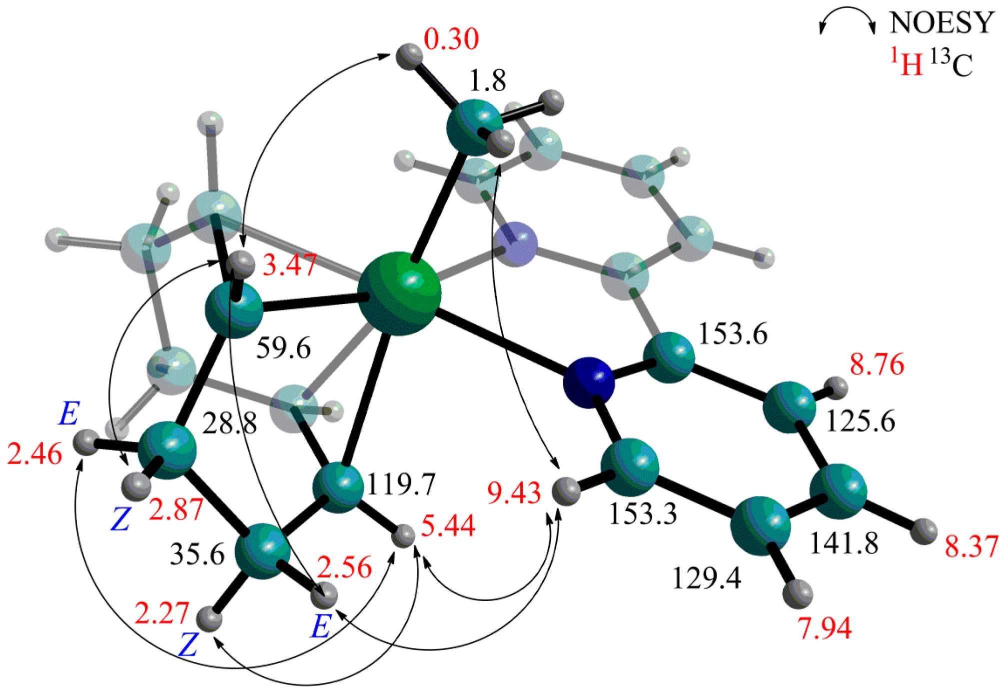


**Figure 3.** $^1$H-$^1$H NOESY spectra of [Pt(bpy)(cod)(Me)][SbF$_6$] in acetone-d$^6$ (600-ms mixing time at 600 MHz, 298 K).



**Scheme 3.** Assignment of $^1$H and $^{13}$C signals and $^1$H-$^1$H NOESY contacts (arrows) superimposed on the molecular structure of [Pt(bpy)(cod)(Me)]$^+$ from single-crystal XRD.

At the low field of the $^1$H NMR spectrum (Figures 2 and 3), four signals represent the four magnetically-independent protons of the bpy ligand in [Pt(bpy)(cod)(Me)]$^+$. Thus, both N atoms bind to the Pt atom in a local $C_s$ symmetry, in line with the molecular structure in the crystal (Figure 1) and the Structures (a), (e) and (f) in Scheme 2. The two olefin protons at 3.5 and 5.5 ppm and the Me coligand (Table 2), respectively, show satellites due to $^2J$Pt–H coupling ($^{195}$Pt with $I$ = ½ and 33.7% nat. abundance). While the signal at 5.5 ppm of one of the olefin groups lies in the normal range for olefin Pt(II) complexes [53–55,94–104], an upfield shift to 3.5 ppm is unusual and has been assigned previously to correspond to an axial olefin ligand in a trigonal bipyramidal configured five coordinate Pt(II) complex [53–55]. In our previous work, we could show that the $^2J$Pt–H coupling constants have been found to be very indicative of the local symmetry around Pt and the *trans* influence of the *trans*-located coligand [94–96]. The signal at 5.5 ppm exhibits a coupling of 31 Hz, indicative of a very strong *trans*-oriented ligand, very probably the Me coligand, e.g., in [Pt(cod)(Me)Cl], the olefin protons *trans* to Me show a $^2J$Pt–H coupling of 36 Hz, while those *trans* to Cl exhibit 75 Hz [95]. The signal at 5.5 ppm shows satellites with a $^2J$Pt–H coupling of 74 Hz, and a weak ligand must be in the *trans* position; presumably, this is bpy. For the pyridine complex [Pt(cod)(Me)(Py)]$^+$, a value of 72 Hz was recorded in the same solvent [44]. The Me signal exhibits a $^2J$Pt–H coupling of 66 Hz. This clearly indicates a *trans*-oriented ligand, thus ruling out Structures (c) and (f) in Scheme 2. In square planar codPt(Me) complexes, this value ranges from 65 to 83 Hz [44,94–96,101–103], putting the observed value at the lower end, which is in line with one of the olefin groups ($X_2$) being this *trans* ligand. Furthermore, at 600 MHz, the cod $CH_2$ groups show four distinct multiplets from 2.2 to 2.9 ppm (Figures 2 and 3). Detailed 2D NMR experiments reveal that the four signals correspond to each proton of two sets of magnetically rather equivalent C atoms (Figure 2 insert). One of these groups shows a marked $^3J$Pt–H coupling of about 60 Hz. This signal corresponds to two protons on two different $CH_2$ groups having a perfect orientation for coupling to Pt. We name these two protons *E* (Scheme 3), using the *E*,*Z* nomenclature for olefins, since the Pt–C–C–H dihedral angles of these two protons lie about 20° (from the crystal structure), thus close to the 0° for two *E* oriented groups in an unsaturated system. The two other protons on these $CH_2$ groups, the *Z* protons, exhibit angles of about 80° and no detectable $^3J$Pt–H coupling. The $^1J$Pt–C coupling to the two olefin groups of 31 Hz for the axial and 334 Hz for the equatorial position, which were comparable to related five coordinate Pt(II) olefin complexes [15,16,48–55,71,72,79,105], also reflects the very different binding strength of the two groups and, thus, strongly suggests a trigonal bipyramidal coordination [15,53–55]. Thus, the NMR data are completely in line with the molecular structure from the XRD and are represented by Structure (a) in Scheme 2. As has been pointed out before, relatively high $^1J$Pt–C for a Pt bound olefin group points to a more pronounced description of the Pt–olefin binding as a metallacyclopropane unit [15]. Very similar values (332–340 Hz) have been reported for the above-mentioned derivatives $[Pt(N^\wedge N')(cod)(Me)]^+$, whereas for the very frequent monoolefin complexes $[Pt(N^\wedge N)(\eta^2\text{-}C_2H_4)Cl_2]$, the $^1J$Pt–C can reach similar values for very bulky N^N diimine ligands [15]. For less bulky diimines and diamines, markedly lower values (<230 Hz) were observed.

The $^{195}$Pt shift of the title complex of −3318 ppm lies in the normal range for Pt(II) complexes. Recently, the $^{195}$Pt shifts of the above-mentioned five coordinate monoolefin complexes $[Pt(N^\wedge N)(\eta^2\text{-}C_2H_4)Cl_2]$ were correlated to the bulkiness of the N^N ligands [15]. Furthermore, the $^{195}$Pt shift decreases constantly in the complexes $[Pt(Me_2phen)(\eta^2\text{-}C_2H_4)X_2]$ along the series X = Cl > Br > I from −2169 to −4041 [16]. However, as Table 2 and previous data show, the $^{195}$Pt shifts for organometallic square planar codPt(II) complexes cover a range from at least 3100 to 3700 ppm [94–104]. Thus, the shift observed for the title complex seems not to be characteristic for the pentacoordination.

Interestingly, in the mixtures of $[Pt(bpy)(cod)(Me)]^+$ and $[Pt(cod)(Me)(OH_2)]^+$ (Table 2, Figure S4), as obtained from initial synthesis, the NMR signals of the five coordinate complex are identical to a pure sample. Thus, the aqua complex seems not to be involved in dynamic processes, such as scrambling with the latter. The $^2J$Pt–H coupling of $[Pt(cod)(Me)(OH_2)]^+$ of the olefin protons *trans* to the $H_2O$ ligand is 88 Hz and smaller than the 91 Hz found for the acetone complex $[Pt(cod)(Me)(acetone)]^+$ [44], which was not observed in the NMR spectra. In terms of bond strength, this indicates that water is a slightly better ligand to Pt than acetone in such complexes. This and the fact that the aqua complex seems to be quite stable in solution might be of importance in view of the ongoing investigations of the thriving, but yet not understood cytotoxicity of such organoplatinum(II) complexes with olefin ligands [94–96,106]. The other olefin protons in $[Pt(cod)(Me)(OH_2)]^+$, located *trans* to the Me coligand, show a $^2J$Pt–H coupling of 35 Hz. The signal for the Me coligand exhibits a $^2J$Pt–H coupling of 66 Hz. An identical value was found for $[Pt(bpy)(cod)(Me)]^+$, which supports the assumption that in the five coordinate complex, the Me coligand faces an olefinic *trans* ligand.

**Table 2.** Selected $^{1}$H and $^{195}$Pt NMR data of cod platinum complexes [a].

| **compound** | **δ H1,2-cod *trans* L (equatorial)** | **$^{2}J$Pt–H H1,2-cod *trans* L** | **δ H5,6-cod *trans* Me (axial)** | **$^{2}J$Pt–H H5,6-cod *trans* Me** | **δ Me** | **$^{2}J$Pt–H Pt–CH$_3$** | **δ $^{195}$Pt** |
|---|---|---|---|---|---|---|---|
| [Pt(cod)(Me)Cl] | 4.54 | 75 | 5.42 | 36 | 0.78 | 73 | −3501 |
| [Pt(bpy)(cod)(Me)]$^{+}$ | 3.48 | 74 | 5.46 | 31 | 0.32 | 66 | −3318 |
| [Pt(cod)(Me)(H$_2$O)]$^{+}$ | 4.96 | 88 | 5.65 | 35 | 0.79 | 66 | −3465 |
| [Pt(cod)(Me)(acetone)]$^{+}$ [b] | 4.95 | 91 | 5.65 | 31 | 0.88 | 64 | −3416 |

[a] $^{1}$H or $^{195}$Pt NMR shifts (ppm) and selected $^{195}$Pt–H coupling constants (Hz), measured in acetone-d$^{6}$. [b] From [44].

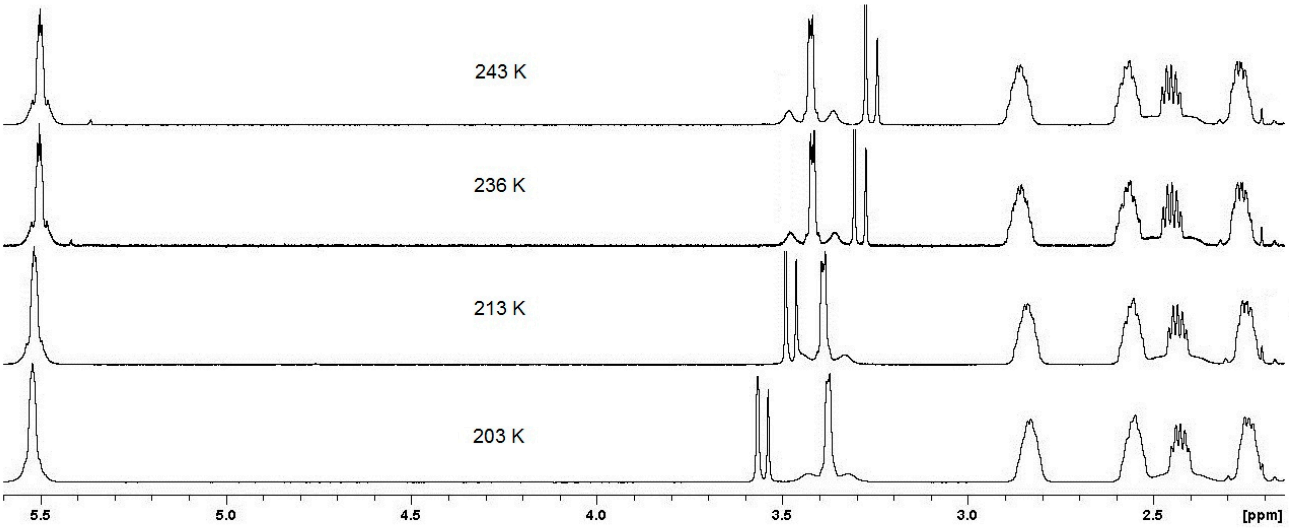


**Figure 4.** $^{1}$H NMR spectra of [Pt(bpy)(cod)(Me)][SbF$_6$] recorded at 600 MHz in acetone-d$^{6}$ at various temperatures. The two singlet signals moving from about 3.3 to 3.55 ppm during cooling represent H$_2$O and DHO, respectively, originating from the solvent [107].

As pointed out above, at ambient temperature in acetone-d$^{6}$ solution, the title complex exhibits two signals of each of two protons for the olefinic groups, indicating the equivalence of the two protons on the axial and the equatorial olefin group, respectively. This has been observed for most of the so far reported square planar codPt complexes and is due to a facile motion of the cod –CH$_2$–CH$_2$– group, rendering the two protons on a –HC=CH– group equivalent. In the solid, this motion is frozen, and consequently, four $^{1}$H signals and also four $^{13}$C signals were observed [105]. Furthermore, for most of the above-mentioned derivatives [Pt(N^N')(cod)(Me)]$^{+}$ with various pyridine-2-iminomethyl-aniline ligands (N^N'), four distinct signals were reported [72]. This can be explained by the unsymmetrical nature of the here used diimine ligands and, thus, supports once more the assumed trigonal bipyramidal structure of these complexes in solution. Interestingly, for the derivative carrying the least bulky N^N' ligand, the olefin signals are merged into two signals at ambient temperature, and the axial signal splits into two at −213 K, while the signal for the equatorial protons remains unchanged. This has been assigned to a dynamic processes involving partial splitting of the N^N' ligand [72]. In contrast to this, the corresponding chloride complexes [Pt(N^N')(cod)Cl]$^{+}$ seem to exhibit fluxional behavior in corresponding NMR experiments due to rearrangements, including partial splitting of the cod ligand [72].

We have studied the NMR behavior of the title complex at low temperatures and 600 MHz (Figure 4). In our experiments, two signals for the olefin protons and four distinct signals for the cod –$CH_2$– groups were detected at temperatures from 303 to 203 K. No merging or splitting of signals occurs within this temperature range; only the $^2J$Pt–H coupling constant of the equatorial olefin protons *trans* to bpy decreases from about 73 Hz to 63 Hz, while the value for the axial olefin protons remains largely constant. This obvious difference between our results and those obtained for the $[Pt(N^\wedge N')(cod)(Me)]^+$ derivatives with unsymmetrical pyridine-2-iminomethyl-aniline ligands [72] might lie in the lower symmetry of these complexes and the bulkiness of those ligands. In future work we will thus synthesize further derivatives of the title complex with more bulky diimine ligands, but also use unsymmetrical cod ligands, such as 1-methyl-2,5-cylooctadiene [106].

## 3. Experimental Section

### 3.1. General

All preparations were carried out in a dry argon atmosphere using Schlenk techniques. Additionally, the preparation of the title complex was carried out in the dark. Solvents ($CH_2Cl_2$, THF, toluene, diethyl ether and MeCN) were dried using a MBRAUN MB SPS-800 solvent purification system.

### 3.2. Instruments

The NMR spectra were recorded on a Bruker Avance II 300-MHz ($^1$H: 300.13 MHz, $^{13}$C: 75.47 MHz) double resonance (BBFO) 5-mm observation probe head with a z-gradient coil, a Bruker Avance 400 spectrometer ($^1$H: 400.13 MHz, $^{13}$C: 100.61 MHz, $^{195}$Pt: 86.01 MHz) triple resonance (TBI) 5-mm inverse probe head with a z-gradient coil and a Bruker Avance II 600 spectrometer ($^1$H: 600.13 MHz, $^{13}$C: 150.93 MHz, $^{15}$N: 60.83 MHz) triple resonance (TBI) 50-mm inverse probe head with z-gradient coil. The broadband coil was tuned to either the carbon or the platinum frequency and the detection coil to the proton frequency, resulting in 90° pulses of 11.9 µs for $^{13}$C, 12.5 µs for $^{195}$Pt and 12.4 µs for $^1$H. The unambiguous assignment of the $^1$H, $^{13}$C and $^{195}$Pt resonances was obtained from $^1$H TOCSY, $^1$H COSY, $^1$H NOESY, gradient-selected $^1$H, $^{13}$C HSQC and HMBC and gradient-selected $^1$H, $^{195}$Pt HMBC experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts were relative to TMS for $^1$H and $^{13}$C, $NH_3$ for $^{15}$N and $Na_2[PtCl_6]$ in $D_2O$ for $^{195}$Pt. The spectra analyses were performed by the Bruker TopSpin 3.2 software. EI-MS spectra were measured using a Finnigan MAT 95. Elemental analyses were carried out on Hekatech CHNS EuroEA 3000 Analyzer. IR spectra were measured on a Bruker IFS66vS.

### 3.3. Reagents

The complex [(COD)Pt(Me)Cl] was prepared according to published procedures [94–96]. All other chemicals were purchased by commercial suppliers and were used without further purification.

### *3.4. Synthesis of [Pt(bpy)(cod)(Me)][SbF$_6$]*

**A Reactions using a sub-stoichiometric amount of bpy (attempted synthesis of [(μ-bpy){Pt(bpy)(Me)}$_2$]$^{2+}$):** In a typical reaction, an amount of 216 mg (0.612 mmol) [Pt(cod)(Me)Cl] was dissolved in 50 mL of (non-dried) acetone, and 210 mg (0.612 mmol) of Ag[SbF$_6$] were added. After stirring for 10 min, the formed precipitate was filtered off, and the filtrate was added to a solution of 55 mg (0.35 mmol; corresponding to a 2:2:1.14 ratio) of 2,2'-bipyridine in acetone. The reaction mixture was heated under reflux for 22 h. After distilling off the solvent, a yellow solid was obtained. NMR spectroscopic investigation showed the presence of the complexes [Pt(bpy)(cod)(Me)]$^+$ and [Pt(cod)(Me)(H$_2$O)]$^+$ in a 6:4 ratio. [Pt(cod)(Me)(OH$_2$)]$^+$: $^1$H NMR (acetone-d$^6$): δ = 5.65 (m, 2H, $^2J$Pt–H = 35 Hz, H5,6cod), 4.96 (m, 2H, $^2J$Pt–H = 88 Hz, H1,2cod), 2.95 to 2.21 (m, 8H, H3,4,7,8cod), 0.79 (s, 3H, $^2J$Pt–H = 66 Hz, MePt) ppm. $^{195}$Pt–$^1$H HMBC (acetone-d$^6$): δ = –3465 ppm.

Further reactions with ratios ranging from 2:2:0.8 to 2:2:1.5 gave corresponding mixtures [Pt(bpy)(cod)(Me)]$^+$ and [Pt(cod)(Me)(H$_2$O)]$^+$.

**B selective synthesis of [Pt(bpy)(cod)(Me)][SbF$_6$]:** An amount of 100 mg (0.282 mmol) [Pt(cod)(Me)Cl] was dissolved in 50 mL of dried THF, and 97 g (0.282 mmol) of Ag[SbF$_6$] were added. After stirring for 10 min, the formed precipitate was filtered off, and the filtrate was added to a solution of 44 mg (0.282 mmol) of 2,2'-bipyridin in THF. The reaction mixture was heated under reflux for 28 h. After distilling off the solvent, a yellow solid was obtained, which was recrystallized from CH$_2$Cl$_2$, yielding 195 mg (0.263 mmol) of yellow microcrystalline material of [Pt(bpy)(cod)(Me)][SbF$_6$]. Yield: 93%. Anal. calcd. for $C_{21}H_{29}F_6N_2Pt_1Sb_1$ (740.30): C 34.07, H 3.46, N 3.78. Found: C 34.08, H 3.46, N 3.79. $^1$H NMR (acetone-d$^6$): δ = 9.42 (d, 2H, $^2J$Pt–H = 22 Hz, H6,6'bpy), 8.76 (d, 2H, H3,3'bpy), 8.37 (d, 2H, H4,4'bpy), 7.94 (d, 2H, H5,5'bpy), 5.44 (m, 2H, $^2J$Pt–H = 25 Hz, H1,2cod), 3.47 (m, 2H, $^2J$Pt–H = 74 Hz, H6,5cod), 2.90 to 2.83 (m, 2H, H4*Z*,8*Z*cod), 2.60 to 2.53 (m, 2H, H3*E*,7*E*cod), 2.48 to 2.42 (m, 2H, $^2J$Pt–H = 70 Hz H4*E*,8*E*cod), 2.29 to 2.24 (m, 2H, H3*Z*,7*Z*cod), 0.30 (s, 3H, $^2J$Pt–H = 66 Hz, MePt) ppm. $^{13}$C NMR (acetone-d$^6$): δ = 153.6 (C2bpy), 153.3 ($^2J$Pt–C = 36 Hz, C6bpy), 141.9 (C4bpy), 129.4 ($^2J$Pt–C = 22 Hz, C5bpy), 125.6 (C3bpy), 119.7 ($^1J$Pt–C = 31 Hz, C1,2cod), 59.6 ($^1J$Pt–C = 334 Hz, C5,6cod), 35.6 ($^2J$Pt–C = 34 Hz, C4,8cod), 28.8 ($^2J$Pt–C = 24 Hz, C3,7cod), 1.8 ($^1J$Pt–C = 595 Hz, $C_{MePt}$) ppm. $^{15}$N NMR (acetone-d$^6$): $\delta$ = 260 (s, 2N, bpy) ppm. $^{195}$Pt–$^1$H HMBC (acetone-d$^6$): δ = –3318 ppm. EI-MS: $m/z$ = 740 [M$^+$].

### *3.5. Crystal Structure Determination*

The data collection was performed at $T$ = 170(2) K on a STOE IPDS II diffractometer with Mo-Kα radiation (λ = 0.71073 Å) employing the ω-2θ scan technique. The structure was solved by direct methods using SIR 92 [108] and WinGX [109], and refinement was carried out with SHELXL2013, employing full-matrix least-squares methods on $F^2$ [110] with $F_0{}^2 \geq 2\sigma(F_0{}^2)$, with the results shown in Table 1 (and the Supplementary Material). All non-hydrogen atoms were treated anisotropically; hydrogen atoms were included by using appropriate riding models. CCDC 1047002 contains the full crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ U.K. Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk.

## 4. Conclusions

The five coordinate organoplatinum complex [Pt(bpy)(cod)(Me)][$SbF_6$] (cod = 1,5-cyclooctadiene, bpy = 2,2'-bipyridine) was obtained reacting [Pt(cod)(Me)Cl] with Ag[$SbF_6$] and bpy and characterized by multiple spectroscopy (IR and NMR) and single-crystal XRD. The molecular structure clearly shows the five coordinate binding. Application of the so-called trigonality index, the $\tau$ value, for the discrimination between trigonal bipyramidal *vs.* square pyramidal coordination gave a value of 0.528, thus largely in-between the two geometries. However, a closer look revealed that chelate bite angles for the bpy ligand (73°) largely distort the basal trigonal plane ($X_1$–Pt–N angles of about 143°), and the cod bite angle (86°) leads to a distortion of the "axial" Me–Pt–X2 angle; both devaluate the $\tau$ value. Nevertheless, the molecular structure can be unequivocally described as basally-distorted trigonal bipyramidal. Based on multinuclear and 2D NMR experiments, a complete picture of the molecular structure in solution could be drawn giving strong evidence for the same structure as found in the crystal.

## Acknowledgments

We are indebted to Ingo Pantenburg (University of Cologne) for single-crystal XRD measurements and Johnson Matthey (JM) for a loan of $K_2PtCl_4$.

## Author Contributions

Axel Klein devised this work and wrote the manuscript. Michael Neugebauer prepared the title complex for the first time and the crystal structure determination was carried out by him and Alexander Krest. Anna Lüning prepared larger amounts of the complex and worked out the preparative routes. Simon Garbe and Natalia Arevyeva did the analytics and carried out the high field and 2D NMR experiments. All NMR experiments were supervised by Nils Schlörer.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Steed, J.W.; Atwood, J.L. *Supramolecular Chemistry*, 2nd ed.; Wiley: Chichester, UK, 2009.
2. Thorn, D.L.; Hoffmann, R. The Olefin Insertion Reaction. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.
3. Garrou, P.E.; Heck, R. The Mechanism of Carbonylation of Halo(bis-ligand)organoplatinum(II), -palladium(II), and -nickel(II) Complexes. *J. Am. Chem. Soc.* **1976**, *98*, 4115–4127.
4. Albano, V.G.; Monari, M.; Orabona, I.; Ruffo, F.; Vitagliano, A. Molecular rearrangements in the formation of five-coordinate platinum(II) olefin complexes. Structural and mechanistic aspects. *Inorg. Chim. Acta* **1997**, *265*, 35–46.

5. Lo, W.K.C.; Cavigliasso, G.; Stranger, R.; Crowley, J.D.; Blackman, A.G. Five-Coordinate $[Pt^{II}(bipyridine)_2(phosphine)]^{n+}$ Complexes: Long-Lived Intermediates in Ligand Substitution Reactions of $[Pt(bipyridine)_2]^{2+}$ with Phosphine Ligands. *Inorg. Chem.* **2014**, *53*, 3595–3605.
6. Fernandez-Anca, D.; Garcia-Seijo, M.I.; Garcia-Fernandez, M.E. Tuneable reactivity with $PPh_3$ and $SnX_2$ of four- and five-coordinate Pd(II) and Pt(II) complexes containing polyphosphines. *Dalton. Trans.* **2013**, *42*, 10221–10232.
7. Bortoluzzi, M.; Paolucci, G.; Pitteri, B.; Zennaro, P.; Bertolasi, V. New platinum(II) and palladium(II) quinoline-imine-pyridine, quinoline-imine-thiazole and quinoline-imine-imidazole complexes by metal-assisted condensation reactions. *J. Organomet. Chem.* **2011**, *696*, 2565–2575.
8. Grant, G J.; Benefield, D.A.; VanDerveer, D.G. Thiacrown $Pt^{II}$ complexes with group 15 donor ligands: pentacoordination in Pt(II) complexes. *Dalton Trans.* **2009**, 8605–8615.
9. Momeni, B.Z.; Baleh, L.J.; Hamzeh, S.; Rominger, F. Insertion of $SnCl_2$ into Pt–Cl bonds: synthesis and characterization of four- and five-coordinate trichlorostannylplatinum(II) complexes *J. Coord. Chem.* **2007**, *60*, 285–293.
10. West, N.M.; Reinartz, S.; White, P.S.; Templeton, J.L. Carbon Monoxide Promoted Reductive Elimination of Hydrogen from Tp’ Platinum Complexes. *J. Am. Chem. Soc.* **2006**, *128*, 2059–2066.
11. MacDonald, M.G.; Kostelansky, C.N.; White, P.S.; Templeton, J.L. Ethylene Insertion in Tp’Pt(Ph)($\eta^2$-$CH_2$=$CH_2$) and C–H Activation of Ethylbenzene to Form a Platinum(IV) *ortho*-Metalated Phenethyl Complex. *Organometallics* **2006**, *25*, 4560–4570.
12. Sagakawa, T.; Ohtsuki, K.; Ishiyma, T.; Ozawa, F. Insertion of Phenylacetylene into $Pt(SnMe_3)_2(PMe_2Ph)_2$. *Organometallics* **2005**, *24*, 1670–1677.
13. Ara, I.; Fornies, J.; Garcia-Monforte, M.A.; Menjon, B.; Sanz-Carillo, R.M.; Tomas, M.; Tsipis, A.C.; Tsipis, C.A. Synthesis and Characterization of New Five-Coordinate Platinum Nitrosyl Derivatives: Density Functional Theory Study of Their Electronic Structure. *Chem. Eur. J.* **2003**, *9*, 4094–4105.
14. Otto, S.; Roodt, A. Five co-ordination at platinum(II) in a water soluble tertiary phosphine complex: crystal structure of $[Pt(PTA)_3(I)_2].CH_3OH$. *Inorg. Chem. Commun.* **2001**, *4*, 49–52.
15. Benedetti, M.; Antonucci, D.; Girelli, C.R.; Fanizzi F.P. Hindrance, Donor Ability of $Me_n$N^N Chelates and Overall Stability of Pentacoordinate $[PtCl_2(\eta^2\text{-}CH_2{=}CH_2)(Me_nN\text{\^{}}N)]$ Complexes as Observed by $\eta^2$-Olefin $^1J$Pt,C Modulation: An NMR Study. *Eur. J. Inorg. Chem.* **2015**, 2308–2316.
16. Benedetti, M.; Papadia, P.; Girelli, C.R.; De Castro, F.; Capitelli, F.; Fanizzi, F.P. X-ray structures *versus* NMR signals in pentacoordinate $[PtX_2(\eta^2\text{-}CH_2{=}CH_2)(Me_2phen)]$ (X = Cl, Br, I) complexes. *Inorg. Chim. Acta* **2015**, *428*, 8–13.
17. Albano, V.G.; De Felice, V.; Monari, M.; Roviello, G.; Ruffo, R. Oxidative Addition of Phenylselenyl Halides to Platinum(0) Complexes: Characterisation and Reactivity of the Products [PtX(SePh)(*N,N*-chelate)(olefin)] (X = Cl, Br, I). *Eur. J. Inorg. Chem.* **2005**, 416–422.
18. De Felice, V.; De Renzi, A.; Fraldi, N.; Roviello, G.; Tuzi, A. C–C coupling of aryl groups and allyl derivatives on Pt(II)-phenanthroline fragments: crystal and molecular structure of the *tbp*

[($\eta^1$,$\eta^2$-2-allyl,5-methyl-phenyl)iodo(1,10-phenanthroline)platinum(II)] complex containing the N–N ligand in axial-equatorial coordination mode. *J. Organomet. Chem.* **2005**, *690*, 2035–2043.

19. Fanizzi, F.P.; Margiotta, N.; Lanfranchi, M.; Tripicchio, A.; Pacchioni, G.; Natile, G. A Molecular Tool for Measuring the Electron-Acceptor Ability of Ligands from Crystallographic Data. *Eur. J. Inorg. Chem.* **2004**, 1705–1713.
20. Albano, V.G.; Monari, M.; Orabona, I.; Panunzi, A.; Ruffo, F. Oxidative Additions of E-E Bonds (E = Chalcogen) to Group 10 Metals: "Tunable" Cleavage of Se-Se Bonds by Pt(0) Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 4352–4353.
21. Benedetti, M.; Barone, C.R.; Girelli, C.R.; Fanizzi, F.P.; Natile, G.; Maresca, L. H/D exchange at $sp^3$ carbons in the coordination sphere of platinum(II). *Dalton Trans.* **2014**, 3669–3575.
22. Plutino, M.R.; Fenech, L.; Stoccoro, S.; Rizzato, S.; Castellano, C.; Albinati, A. Dynamic NMR Study of Ethene Exchange in Cationic CNN-Type Platinum(II) Complexes. *Inorg. Chem.* **2010**, *49*, 407–418.
23. Shiotsuki, M.; White, P.S.; Brookhart, M.; Templeton, J.L. Mechanistic Studies of Platinum(II)-Catalyzed Ethylene Dimerization: Determination of Barriers to Migratory Insertion in Diimine Pt(II) Hydrido Ethylene and Ethyl Ethylene Intermediates. *J. Am. Chem. Soc.* **2007**, *129*, 4058–4067.
24. Reinartz, S.; White, P.S.; Brookhart, M.; Templeton, J.L. Acid-Assisted Reductive Elimination as a Route to Platinum(II) Products from Platinum(IV) Tris(pyrazolyl)borate Reagents. *Organometallics* **2000**, *19*, 3854–3866.
25. Mc Cartney, D.; Guiry, P.J. The asymmetric Heck and related reactions. *Chem. Soc. Rev.* **2011**, *40*, 5122–5150.
26. Lepski, R.; Lüning, A.; Stirnat, K.; Klein, A. Unexpected formation of [($Me_2$-Xyl-DAB)Pd ($\eta^{3-6}$-methyloct-2-en-1-id)][$SbF_6$] ($Me_2$-Xyl-DAB = 2,3-dimethyl-1,4-bis(2,6-dimethylphenyl)-diazabuta-1,3-diene). *J. Organomet. Chem.* **2014**, *751*, 821–825.
27. Estevez, L.; Tuxworth, L.W.; Sotiropoulos, J.-M.; Dyer, P.W.; Miqueu, K. Combined DFT and experimental studies of C–C and C–X elimination reactions promoted by a chelating phosphine–alkene ligand: the key role of penta-coordinate $Pd^{II}$. *Dalton Trans.* **2014**, *43*, 11165–11179.
28. Tuxworth, L.; Baiget, L.; Phanopoulus, A.; Metters, O.J.; Batsanov, A.S.; Fox, M.A.; Howard, J.A.K.; Dyer, P.W. Phosphine–alkene ligand-mediated alkyl–alkyl and alkyl–halide elimination processes from palladium(II). *Chem. Commun.* **2012**, *48*, 10413–10415.
29. McDonald, R.I.; Liu, G.; Stahl, S.S. Palladium(II)-Catalyzed Alkene Functionalization via Nucleopalladation: Stereochemical Pathways and Enantioselective Catalytic Applications. *Chem. Rev.* **2011**, *111*, 2981–3019.
30. Jira, R. Acetaldehyde from ethylene—A Retrospective on the Discovery of the Wacker Process. *Angew. Chem. Int. Ed.* **2009**, *48*, 9034–9037.
31. Keith, J.A.; Henry, P.M. The Mechanism of the Wacker Reaction: A Tale of Two Hydroxypalladations. *Angew. Chem. Int. Ed.* **2009**, *48*, 9038–9049.
32. Hintermann, L. Wacker Oxidation. In *Handbook of C–H Transformations*; Wiley-VCH: Weinheim, Germany, 2005; Volume 1, pp. 287–301.
33. Zeise, W.C. Von der Wirkung zwischen Platinchlorid und Alkohol, und von den dabei entstehenden neuen Substanzen. *Ann. Phys. Chem.* **1831**, *97*, 497–541 (In Germany).

34. Hunt, L.B. The First Organometallic Compounds. *Plat. Met. Rev.* **1984**, *28*, 76–83.
35. Nyholm, R.S. Synthesis, Structure and Reactions of Chelate Metal-Olefin Complexes. *Pure Appl. Chem.* **1971**, *27*, 127–144.
36. Nyholm, R.S. Electron Configuration and Structure of Transition-Metal Complexes. *Proc. Chem. Soc.* **1961**, 273–296.
37. Benedetti, M.; Barone, C.R.; Antonucci, D.; Vechio, V.M.; Ienco, A.; Maresca, L.; Natile, G.; Fanizzi, F.P. Modulation of properties in analogues of Zeise's anion on changing the ligand trans to ethene. X-ray crystal structures of *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$ and *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$. *Dalton Trans.* **2012**, *41*, 3014–3021.
38. Chock, P.B.; Halpern, J.; Paulik, F.E.; Shupack, S.I.; DeAngelis, T.P. Potassium Trichloro(ethene)palatinate(II) (Zeise's salt). *Inorg. Synth.* **1990**, *28*, 349–351.
39. Love, R.A.; Koetzle, T.F.; Bau, R. Neutron Diffraction Study of the Structure of Zeise's Salt, $KPtCl_3(C_2H_4)$ $H_2O$. *Inorg. Chem.* **1975**, *14*, 2653–2657.
40. Black, M.; Mais, R.H.B.; Owston, P.G. The Crystal and Molecular Structure of Zeise's Salt, $KPtCl_3$ $C_2H_4.H_2O$. *Acta Crystallogr. B* **1969**, *25*, 1753–1759.
41. Birnbaum, K. Ueber die Einwirkung der schwefligen Saure auf Platinchlorid. *Ann. Chem. Pharm.* **1869**, *152*, 137–147.
42. Benedetti, M.; Antonucci, D.; de Pascali, S.A.; Ciccarella, G.; Fanizzi, F.P. Alkyl-vinyl-ethers from alcoholic substrates and the Zeise's salt, via square planar $[PtCl(N\hat{}N)(\eta^1\text{-}CH_2CH_2OR)]$ complexes. *J. Organomet. Chem.* **2012**, *714*, 104–108.
43. Benedetti, M.; Fanizzi, F.P.; Maresca, L.; Natile, G. The unexpected reactivity of Zeise's anion in strong basic medium discloses new substitution patterns at the platinum centre. *Chem. Commun.* **2006**, 1118–1120.
44. Klein, A.; Klinkhammer, K.-W.; Scheiring, T. Cyclooctadienemethylplatinum complexes: synthesis, reactivity, molecular structure and spectroscopic properties of the organometallic hydroxoplatinum(II) complex [(COD)PtMe(OH)] *J. Organomet. Chem.* **1999**, *592*, 128–135.
45. Rooke, D.A.; Menard, Z.A.; Ferreira, E.M. An analysis of the influences dictating regioselectivity in platinumcatalyzed hydrosilylations of internal alkynes. *Tetrahedron* **2014**, *70*, 4232–4244.
46. Dub, P.A.; Daran, J.-C.; Levin, V.A.; Belkova, N.V.; Shubina, E.S.; Poli, R. Modeling the platinum-catalyzed intermolecular hydroamination of ethylene: The nucleophilic addition of $HNEt_2$ to coordinated ethylene in *trans*-$PtBr_2(C_2H_4)(HNEt_2)$. *J. Organomet. Chem.* **2011**, *696*, 1174–1183.
47. Karshtedt, D.; Bell, A.T.; Don Tilley, T. Platinum-Based Catalysts for the Hydroamination of Olefins with Sulfonamides and Weakly Basic Anilines. *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646.
48. Benedetti, M.; Antonucci, D.; Girelli, C.R.; Capitelli, F.; Fanizzi, F.P. Reactivity of $[PtCl(\eta^2\text{-}C_2H_4)(N\text{-}N)]^+$, N-N = diimine ligand, with phenol derivatives and first comparison between single crystal X-ray structures of *syn*- and *anti*-$[Pt(N\text{-}N)(phenolate)_2]$ rotamers in the solid state. *Inorg. Chim. Acta* **2014**, *409*, 427–432.

49. Benedetti, M.; Girelli, C.R.; Antonucci, D.; De Pascali, S.A.; Fanizzi, F.P. New method for the synthesis of [PtCl{$\eta^1$-$CH_2C(O)R$}(N-N)] ketonyl derivatives starting from the Zeise's salt. *Inorg. Chim. Acta* **2014**, *413*, 109–114.
50. Benedetti, M.; Girelli, C.R.; Antonucci, D.; Fanizzi, F.P. [PtCl($\eta^1$-$CH_2$–$CH_2OR$)(N^N)] and [PtCl($\eta^2$-$CH_2$=$CH_2$)(N^N)]$^+$, N^N = dinitrogen ligand, complexes. Sterical and electronic effects evidenced by NMR analysis. *J. Organomet. Chem.* **2014**, *771*, 40–46.
51. Benedetti, M.; Antonucci, D.; de Pascali, S.A.; Girelli, C.R.; Fanizzi, F.P. Pentacoordinate [$PtCl_2$($\eta^2$-$C_2H_4$)(N-N')] complexes with asymmetrically hindered nitrogen donor chelates. Stereospecific synthesis of *syn*- and *anti*-[PtCl($\eta^1$-$CH_2CH_2OMe$)(Mebpy)]. *J. Organomet. Chem.* **2012**, *714*, 60–66.
52. Barone, C.R.; Benedetti, M.; Vecchio, V.M.; Fanizzi, F.P.; Maresca, L.; Natile, G. New chemistry of olefin complexes of platinum(II) unravelled by basic conditions: synthesis and properties of elusive cationic species. *Dalton Trans.* **2008**, 5313–5322.
53. Albano, V.G.; Natile, G.; Panunzi, A. Five-coordinate platinum(II). *Coord. Chem. Rev.* **1994**, *133*, 67–114.
54. Maresca, L.; Natile, G. Five-Coordination in Platinum(II) and Palladium(II) Chemistry. *Comments Inorg. Chem.* **1993**, *16*, 95–112.
55. Fanizzi, F.P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. Five-coordination in Platinum(II) Species: When and Why. *J. Chem. Soc. Chem. Commun.* **1992**, 333–335.
56. Margiotta, N.; Bertolasi, V.; Capitelli, F.; Maresca, L.; Moliterni, A.G.G.; Vizza, F.; Natile, G. Influence of steric and electronic factors in the stabilization of five-coordinate ethylene complexes of platinum(II): X-ray crystal structure of [$PtCl_2$(2,9-dimethyl-1,10-phenanthroline-5,6-dione)]. *Inorg. Chim. Acta* **2004**, *357*, 149–158.
57. De Felice, V.; De Renzi, A.; Ferrara, M.L.; Panunzi, A. Reaction products of CO with square-planar platinum(II)-(*N*,*N*-chelate) complexes: synthesis and reactivity. *J. Organomet. Chem.* **1996**, *513*, 97–104.
58. Bartolucci, S.; Carpinelli, P.; De Felice, V.; Giovannitti, B.; De Renzi, A. Five-coordinate platinum(II) complexes containing substituted olefins: synthesis and cytostatic activity. *Inorg. Chim. Acta* **1992**, *197*, 51–57.
59. Fanizzi, F.P.; Intini, F.P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. Four- *versus* Five-co-ordination in Palladium(II) and Platinum(II) Complexes containing 2,9-Dimethyl-l,10-phenanthroline (dmphen). Crystal Structures of [$PtCl_2$(dmphen)] and [Pt($\eta^2$-$C_2H_4$)$Cl_2$(dmphen)]. *J. Chem. Soc., Dalton Trans.* **1991**, 1007–1015.
60. Natile, G.; Maresca, L.; Cattalini, L.; Belluco, U.; Uguagliati, P.; Croatto, U. Decomposition of [Pt($C_2H_4$)$Cl_2$(bipyridyl)] to [$PtCl_2$(bipyridyl)] and Ethylene in Different Solvents. *Inorg. Chim. Acta* **1976**, *20*, 49–52.
61. De Pascali, S.A.; Migoni, D.; Papadia, P.; Muscella, A.; Marsigliante, S.; Ciccarese, A.; Fanizzi, F.P. New water-soluble platinum(II) phenanthroline complexes tested as cisplatin analogues: First-time comparison of cytotoxic activity between analogous four- and five-coordinate species. *Dalton Trans.* **2006**, 5077–5087.

62. Fanizzi, F.P.; Maresca, L.; Pacifico, C.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. Halogenation of Alkenes in Five-Coordinate Platinum(II) Complexes—Route to Stable (β-Haloalkyl) platinum(IV) Species. *Eur. J. Inorg. Chem.* **1999**, 1351–1358.
63. Fanizzi, F.P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. Five-coordinate platinum(II) alkyne complexes: synthesis, ab initio calculations and crystal and molecular structure of $[PtI_2(Me_2phen)(\eta^3\text{-}PhC{\equiv}CPh)]\cdot CHCl_3$. *Inorg. Chim. Acta* **1998**, *275–276*, 500–509.
64. Fanizzi, F.P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Laschi, F.; Zanello, P. Steric Crowding and Redox Reactivity in Platinum(II) and Platinum(IV) Complexes Containing Substituted 1,10-Phenanthrolines. *Inorg. Chem.* **1996**, *35*, 3173–3182.
65. Clark, R.J.H.; Fanizzi, F.P.; Natile, G.; Pacifico, C.; van Rooyen, C.G.; Tocher, D.A. Steric constraints and addition reactions in platinum(II) complexes containing 2,9-dimethyl-l,10-phenanthroline($Me_2$-phen). X-ray crystal structures of [$PtBr_2$($Me_2$-phen)] and [$PtI_2$($Me_2$-phen)]. *Inorg. Chim. Acta* **1995**, *235*, 205–213.
66. Centore, R.; Roviello, G.; Tuzi, A. Two geometrical isomers of the five-coordinate Platinum(II) complex [PtBr(SePh)(2,9-dimethyl-1,10-phenanthroline)(dimethylmaleate)]. *Inorg. Chim. Acta* **2005**, *358*, 2112–2116.
67. De Felice, V.; Giordano, F.; Orabona, I.; Tesauro, D.; Vitagliano, A. Stabilization of unstable unsaturated molecules in five-coordinate TBP complexes of Pt(II): enol, diol and dialdehyde derivatives. *J. Organomet. Chem.* **2001**, *622*, 242–250.
68. Albano, V.G.; Castallari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. Synthesis and Characterization of Five-Coordinate $[PtCl(L)(N\text{-}N)(olefin)]^+$ Complexes. Molecular Structure of [PtCl(pyridine)(2,9-dimethyl-l,10-phenanthroline)(ethylene)]($CF_3SO_3$). *Organometallics* **1992**, *11*, 3665–3669.
69. Sanchez, A.; Castellari, C.; Panunzi, A.; Vitagliano, A.; De Felice, V. New cationic five-coordinate monoolefin in hydrocarbyl complexes of platinum(II). *J. Organomet. Chem.* **1990**, *388*, 243–252.
70. Gund, A.; Keppler, B.K.; Nuber, B. Five-Coordinate Platinum Olefin Complexes: Synthesis, $^1$H NMR Investigations, and Crystal Structure of a Platinum $\eta^2$-Ethylene Crown Ether Complex. *Inorg. Chem.* **1995**, *34*, 2788–2790;
71. Van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C.H. Five-Coordinate $[Pt^{II}Cl_2(\eta^2\text{-olefin})L_2]$ ($L_2$ = σ,σ*N*,*N*'-Bonded α-Diimine or N,N'-Disubstituted 1,2-Diaminoethane) Complexes. Solution Conformation, $\eta^2$-Olefin Rotational Barriers (NMR), and the X-ray Molecular Structure of [$PtCl_2$($\eta^2$-styrene) (*t*-Bu-N=CHCH=N-*t*-Bu)]. *Inorg. Chem.* **1981**, *20*, 2941–2950.
72. Di Bianca, F.; Bandoli, G.; Dolmella, A.; Antonaroli, S.; Crociani, B. Five-coordinate complexes of palladium(II) and platinum(II) with α-diimine and 1,5-cyclooctadiene ligands. *J. Chem. Soc. Dalton Trans.* **2002**, 212–217.
73. Burger, P.; Baumeister, J.M. Transition metal complexes with sterically demanding ligands. I. Synthesis and X-ray crystal structure of 1,5-cyclooctadiene palladium methyl triflate, (COD)Pd(Me)(OTf) and its cationic penta-coordinate adducts with sterically demanding 2,9-diaryl-substituted 1,10-phenanthroline ligands. *J. Organomet. Chem.* **1999**, *575*, 214–222.
74. Albano, V.G.; Demartin, F.; De Felice, V.; Morelli, G.; Vitagliano, A. Five-coordinate diene complexes of platinum(II). *Gazz. Chim. Ital.* **1987**, *117*, 437–441.

75. Rotondo, E.; Tresoldi, G.; Faraone, F.; Pietropaolo, R. Displacement of Dienes from Planar Complexes. 1. Reaction of (1,5-Cyclooctadiene)dichloropalladium(II) with 2,2'-Bipyridyl. *Inorg. Chem.* **1976**, *15*, 2102–2107.
76. De Felice, V.; Cucciolito, M.E.; De Renzi, A.; Ruffo, F.; Tesauro, D. Cationic Platinum(II)-or Palladium(II)-carbyl complexes and unsaturated substrates: a facile way to C–C bond formation. *J. Organomet. Chem.* **1995**, *493*, 1–11.
77. Pietropaolo, R.; Cusmano, F.; Rotondo, E.; Spadaro, A. Preparation and Reactions of Palladium(II) and Platinum(II) Dienyl Complexes. *J. Organomet. Chem.* **1978**, *155*, 117–122.
78. Haszeldine, R.N.; Parish, R.V.; Robbins, D.W. Reactions involving Transition Metals. Part XI. Reactions of Nucleophiles with Dieneplatinum Complexes. *J. Chem. Soc., Dalton Trans.* **1976**, 2355–2363.
79. Overbosch, P.; van Koten, G.; Grove, D.M.; Spek, A.L.; Duisenberg, A.J.M. (Tetraazabutadiene)platinum Complexes. X-ray Crystal and Molecular Structure of the Triethylphosphine Nucleophilic Addition Product $[Pt(1,4\text{-}(4\text{-}NO_2C_6H_4)_2N_4)(CHC(PEt_3)H(CH_2)_2CH{=}CHCH_2CH_2)(PEt_3)]$, a Novel Five-Coordinate Blue Mononuclear Platinum Species. *Inorg. Chem.* **1982**, *21*, 3253–3260.
80. Suzaki, Y.; Osakada, K. Formation, Dynamic Behavior, and Chemical Transformation of Pt Complexes with a Rotaxane-like Structure. *Chem. Asian J.* **2006**, *1*, 331–343.
81. Kretschmer, M.; Pregosin, P.S.; Rüegger, H. Synthesis, $^{119}$Sn, $^{13}$C and $^{195}$Pt NMR Studies of Five-Coordinate Rhodium(I), Iridium(I) and Platinum(II) Complexes Containing Three Trichlorostannate Ligands. *J. Organomet. Chem.* **1983**, *241*, 87–98.
82. Mink, L.; Rettig, M.F.; Wing, R.M. Trigonal-bipyramidal five-coordinate trisolefin complexes of platinum(II). *J. Am. Chem. Soc.* **1991**, *113*, 2065–2071.
83. Herberhold, M.; Schmalz, T.; Milius, W.; Wrackmeyer, B. Tri(1-cyclohepta-2,4,6-trienyl)-phosphine, $P(C_7H_7)_3$, as a tripodal tetradentate ligand in cationic, five-coordinate complexes of platinum(II) and palladium(II). *Z. Naturforsch. B* **2002**, *57*, 255–258.
84. Clark, H.C.; von Werner, K. *cis*-π-Acetylenic Methylplatinum(II) Complexes. *J. Organomet. Chem.* **1975**, *101*, 347–358.
85. Mikola, M.; Klika, K.D.; Hakala, A.; Arpalahti, J. Substitution Reactions of Platinum(II)-Nucleobase Complexes by Associative Mechanism Involving Pseudorotation of the Five-Coordinate Intermediate. *Inorg. Chem.* **1999**, *38*, 571–578.
86. Mikola, M.; Vihanto, J.; Arpalahti, J. Dissociation of Platinum(II) Nucleobase Complexes-Evidence for a Three-path Mechanism via a Five-coordinate Intermediate. *J. Chem. Soc., Chem. Commun.* **1995**, 1759–1760.
87. Klein, A.; Lepski, R. 2,2'-Bipyridine as both Bridging and Terminal Ligand in the Binuclear Palladium Complex $[(\mu\text{-}\eta^1,\eta^1\text{-bpy})\{Pd(Me)(bpy)\}_2](SbF_6)_2$—Structure and Spectroscopic Properties. *Z. Anorg. Allgem. Chem.* **2009**, *635*, 878–884.
88. Crans, D.C.; Tarlton, M.L.; McLauchlan, C.C. Trigonal Bipyramidal or Square Pyramidal Coordination Geometry? Investigating the Most Potent Geometry for Vanadium Phosphatase Inhibitors. *Eur. J. Inorg. Chem.* **2014**, 4450–4468.

89. Addison, A.W.; Rao, T.N.; Reedijk, J.; van Rijn, J.; Verschoor, G.C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[l,7-bis(*N*-methylbenzimidazol-2’-yl)-2,6-dithiaheptane]copper(II) Perchlorate. *Dalton Trans.* **1984**, 1349–1356.
90. Corona-Rodriguez, M.; Hernandez-Ortega, S.; Valdes-Martinez, J.; Morales-Morales, D. [2,2’-Bipyridyl]platinum(II) Complexes with Fluorinated Benzenethiolate Ligands: Synthesis and Structural Elucidation. *Supramol. Chem.* **2007**, *19*, 579–585.
91. Klein, A.; van Slageren, J.; Zalis, S. Co-Ligand Involvement in Ground and Excited States of Electron-Rich (Polypyridyl)$Pt^{II}$ Complexes. *Eur. J. Inorg. Chem.* **2003**, 1927–1938.
92. Textor, M.; Oswald, H.R. Röntgenographische und spektroskopische Untersuchungen an zwei Modifikationen von Dichloro-2,2’-dipyridyl-platin(II). *Z. Anorg. Allgem. Chem.* **1974**, *407*, 244–256.
93. Osborn, R.S.; Rogers, D. Crystal Structure of the Red Form of 2,2’-Bipyridyldichloroplatinum(II). *Dalton Trans.* **1974**, 1002–1004.
94. Lüning, A.; Neugebauer, M.; Lingen, V.; Krest, A.; Stirnat, K.; Deacon, G.B.; Drago, P.R.; Ott, I.; Schur, J.; Pantenburg, I.; Meyer, G.; Klein, A. Platinum Diolefin Complexes—Synthesis, Structures, and Cytotoxicity. *Eur. J. Inorg. Chem.* **2015**, 226–239.
95. Klein, A.; Lüning, A.; Ott, I.; Hamel, L.; Neugebauer, M.; Butsch, K.; Lingen, V.; Heinrich, F.; Elmas, S. Organometallic palladium and platinum complexes with strongly donating alkyl coligands—Synthesis, structures, chemical and cytotoxic properties. *J. Organomet. Chem.* **2010**, *695*, 1898–1905.
96. Butsch, K.; Elmas, S.; Sen Gupta, N.; Gust, R.; Heinrich, F.; Klein, A.; von Mering, Y.; Neugebauer, M.; Ott, I.; Schäfer, M.; Scherer, H.; Schurr, T. Organoplatinum(II) and -palladium(II) Complexes of Nucleobases and Their Derivatives. *Organometallics* **2009**, *28*, 3906–3915.
97. Keefer, C.E.; Bereman, R.D.; Purrington, S.T; Knight, B.W.; Boyle, P.D. The $^{195}$Pt NMR of $L_2Pt$(1,2-dithiolene) Complexes. *Inorg. Chem.* **1999**, *38*, 2294–2302.
98. Rivera, B.; Torrens, H.; Bernès, S. [(1,2:5,6-η)-Cycloocta-1,5-diene]bis[2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzenethiolato]platinum(II). *Acta Cryst. E* **2006**, *62*, m3287–m3288.
99. Osakada, K.; Hosoda, T.; Yamamoto, T. Kinetic Results and Reaction Pathways of Intermolecular Thiolato Ligand Migration between Titanocene Complexes and from $Cp_2TiX(SAr)$ (X = Cl, SAr) to PtCl(Me)(cod) (cod = $\eta^2,\eta^2$-1,5-Cyclooctadiene). *Bull. Chem. Soc. Jpn.* **2000**, *73*, 923–930.
100. Syed, A.; Stevens, E.D.; Cruz, S.G. Reexamination of the σ Bonding in Dichloro(cycloocta-1,5-diene)platinum. *Inorg. Chem.* **1984**, *23*, 3673–3674.
101. Otto, S. Structure and solution behaviour of cyclooctadiene complexes of platinum(II). *Inorg. Chim. Acta* **2010**, *363*, 3316–3320.
102. Suzaki, Y.; Osakada, K. Transmetalation of Phenylplatinum(II) Complex. Isolation and Characterization of a Dinuclear Intermediate in Intermolecular Phenyl Ligand Transfer. *Organometallics* **2004**, *23*, 5081–5084.
103. Smith, D.C., Jr.; Haar, C.M.; Stevens, E.D.; Nolan, S.P. Synthetic, Structural, and Solution Calorimetric Studies of $Pt(CH_3)_2(PP)$ Complexes. *Organometallics* **2000**, *19*, 1427–1433.

104. Wyrwa, R.; Poppitz, W.; Görls, H. Mass Spectrometric and X-Ray Studies on Complexes of the Type (COD)$PtX_2$ (X = Cl, Br, I, $CH_3$, $CH_2CMe_3$, $CH_2SiMe_3$). *Z. Anorg. Allgem. Chem.* **1997**, *623*, 649–653.
105. Gay, I.D.; Young, G.B. Chemical Shift Anisotropy of Organometallic Carbon. *Organometallics* **1996**, *15*, 2264–2269.
106. Enders, M.; Görling, B.; Braun, A.B.; Seltenreich, J.E.; Reichenbach, L. F.; Rissanen, K.; Nieger, M.; Luy, B.; Schepers, U.; Bräse, S. Cytotoxicity and NMR Studies of Platinum Complexes with Cyclooctadiene Ligands. *Organometallics* **2014**, *33*, 4027–4034.
107. Gottlieb, H.E.; Kotlyar, V.; Nudelman, A. NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *J. Org. Chem.* **1997**, *62*, 7512–7515.
108. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.C.; Polidori, G.; Camalli, M. *Sir-92*; A Program for Automatic Solution and Refinement of Crystal Structures; CNR Institute of Crystallography: Bari, Italy, 1994.
109. Farrugia, L.J. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
110. Sheldrick, G.M. *SHELXL-2013*; Program for the Refinement of Crystal Structures; University of Göttingen, Germany, 2008.