

Editorial

Stayin' Alive—Organoplatinum Complexes

Axel Klein

Department of Chemistry, Institute for Inorganic Chemistry, University of Cologne, Greinstrasse 6, D-50939 Cologne, Germany; E-Mail: axel.klein@uni-koeln.de; Tel.: +49-221-470-4006; Fax: +49-221-470-4899

Academic Editor: Duncan Gregory

Received: 23 April 2015 / Accepted: 12 May 2015 / Published: 19 May 2015

Abstract: Starting very early, with the findings of Zeise, or Pope and Peachey, organoplatinum complexes were studied intensely in the 1970s and 1980s and were found to be quite stable and very versatile. From then on, the number of publications on organoplatinum complexes has more than doubled in each subsequent decade, and organoplatinum complexes have stretched into many fields of application today. This introduction to the Special Issue on “Organoplatinum Complexes” spans from the history of organoplatinum complexes to the seven manuscripts published in the frame of this Special Issue, representing some of these fields.

Some say that the 1970s and 1980s of the last century were dull and boring. This might possibly be true for pop music or arts but surely not appropriate for organoplatinum complexes. Those were the days when organoplatinum chemistry received a real boost. Scientific giants, such as Joseph Chatt, F. Gordon A. Stone, Michael Green, Wolfgang Beck, Howard C. Clark, Richard J. Puddephatt, Umberto Belluco, Hans Albert Brune, and Bernard L. Shaw, were active at that time, together with the “next generation”, Martin A. Bennett, George M. Whitesides, Giovanni Natile, Rafael Uson, Raffaello Romeo, and Gerard van Koten, just to name a few. However, organoplatinum chemistry started as early as the 19th century, with reports on the so-called Zeise’s salt $[\text{Pt}(\text{CH}_2\text{CH}_2)\text{Cl}_3]\text{Cl}$, after William Christopher Zeise [1–8], or the heterocubane $[\text{Pt}(\text{Me})_3\text{Cl}]_4$ by W.J. Pope and S.J. Peachey [6,9–13]. This “early success” can be simply rationalized by the fact that platinum, especially in the oxidation state +II, provides very inert and thermodynamically stable Pt–C bonds and Pt^{2+} is (besides Pd^{2+}) the best ion to coordinate to olefin ligands [1,14].

Many of today's applications of organoplatinum compounds, e.g., as building blocks in materials make use of this robustness, which is even elevated in cyclometalated compounds or units. In turn, the ease of the metalation reaction, activating H–C or X–C functions, opens a vast field of synthetic organometallic chemistry. Organometallic platinum complexes or building blocks can be used perfectly to construct supramolecular aggregates or hybrid materials. The most frequent application of such materials lies in their easily tuneable (electro)luminescence. Here, the heavy and relativistic character of platinum and, thus, the availability of triplet-excited states add to the stable binding in such compounds.

The inertness of the Pt–C bond of organoplatinum compounds has also allowed them to enter the field of medicinal chemistry. An increasing number of reports have appeared in the last decades, reporting no marked protonation of such compounds (no loss of the organo ligand) under physiological conditions and increased cytotoxicity compared to the established (non-organometallic) drug cisplatin, while the mechanism of the toxicity seems to be different from the latter.

Finally, chemists would not be chemists if they could not tune the bond strength and reactivity of Pt–C bonds and render them more reactive. Thus, in addition to the established use of organoplatinum complexes as slow models in processes catalyzed by platinum group metals (palladium and rhodium are far less inert), platinum compounds themselves have entered the stage as reactive, chemo- or stereoselective homogeneous catalysts in important organometallic catalytic processes. Nevertheless, a great deal of modeling of organometallic catalysis is carried out studying Pt derivatives in lieu of the assumed organopalladium species. It is not only the higher inertness of the Pt complexes, compared to their palladium derivatives, which allows one to isolate them and study the underlying reaction in stoichiometric variants; the lower reactivity, combined with the unique property of a relatively highly abundant NMR detectable nucleus (^{195}Pt ; $I = 1/2$; natural abundance 33.8%) make Pt containing species detectable even if they occur in mixtures and/or with relatively low abundance.

The contributions in this Special Issue demonstrate the vigor of organoplatinum chemistry today, or in other words, why organoplatinum complexes are “stayin’ alive”.

In the first contribution, Margarita Crespo gives an account of her recent work devoted to the synthesis of cyclometalated Pt(II) and Pt(IV) complexes [15]. Diarylplatinum(II) complexes, such as $[\text{Pt}(\text{aryl})_2(\text{SMe}_2)_2]$, can be used in reactions with *N*-donor ligands carrying suitable adjacent C–H functionalities to produce a variety of cycloplatinated compounds including *endo*-five-, *endo*-six-, *endo*-seven-, or *exo*-five-membered platinacycles. One of the two initial aryl groups on Pt deprotonates the target ligand, cleaving aryl–H, while the other one remains on the Pt atom. Additionally, more complicated reactions were observed when reacting diarylplatinum(II) precursors with suitable ligands including oxidative addition/reductive elimination sequences, involving C–X ($X = \text{H}, \text{Cl}, \text{Br}$) bond activation and, in some cases, C(aryl)–C(aryl) bond formation. Mechanistic details are discussed in this review.

In a more classical way, using non-organometallic *cis*- $[\text{PtCl}_2(\text{dmsO})_2]$ and enantiopure ferrocenyl Schiff base ligands (S_C)- $[\text{FcCH}=\text{N}-\text{CH}(\text{Me})(\text{C}_6\text{H}_5)]$ (**1**) (Fc = ferrocenyl) Concepción López, Ramón Bosque and coworkers have obtained new chiral Pt(II) complexes [16]. One of them is the enantiomerically pure *trans*- (S_C) - $[\text{Pt}\{\kappa^1-N[\text{FcCH}=\text{N}-\text{CH}(\text{Me})(\text{C}_6\text{H}_5)]\}\text{Cl}_2(\text{dmsO})]$ in which the imine acts as a neutral *N*-donor ligand; while the others are the cycloplatinated complexes $[\text{Pt}\{\kappa^2-C,N[(\text{C}_6\text{H}_4)-\text{N}=\text{CHFc}]\}\text{Cl}(\text{dmsO})]$ and the two diastereomers $\{(S_p, S_C)$ and $(R_p, S_C)\}$ of $[\text{Pt}\{\kappa^2-C,N[(\eta^5-C_5H_3)-\text{CH}=\text{N}-\{\text{CH}(\text{Me})(\text{C}_6\text{H}_5)\}]\text{Fe}(\eta^5-C_5H_5)\}\text{Cl}(\text{dmsO})]$. Additionally, the PPh_3 derivatives $[\text{Pt}\{\kappa^2-C,N[(\text{C}_6\text{H}_4)-$

$\text{N}=\text{CHFc}\}]\text{Cl}(\text{PPh}_3)]$ and the diastereomers (S_p, S_C) and (R_p, S_C) of $[\text{Pt}\{\kappa^2\text{-C}, \text{N}[(\eta^5\text{-C}_5\text{H}_5)\text{-CH}=\text{N}\{\text{CH}(\text{Me})(\text{C}_6\text{H}_5)\}]\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}\text{Cl}(\text{PPh}_3)]$ were synthesized. Selected samples of these complexes were submitted for comparative studies of the electrochemical properties and cytotoxic activities on MCF7 and MDA-MB231 breast cancer cell lines. The new complexes exhibit largely ferrocene-centered oxidation processes at rather low potentials. Decreasing potentials seem to go along with increasing cytotoxicity. DFT calculations support this surprising correlation.

A very special type of cyclometalated Pt complexes, so-called half-lantern complexes, were presented by Violeta Sicilia and coworkers [17]. New half-lantern complexes of Pt(II) $[\text{Pt}_2(\mu\text{-L})_2(\text{bzq})_2]$ (Hbzq = benzo[h]quinoline; HL = 4-(trifluoromethyl)pyrimidine-2-thiol) were obtained from the precursor $[\text{Pt}(\text{bzq})(\text{MeCN})_2]\text{ClO}_4$ and 4-(trifluoromethyl)pyrimidine-2-thiol in the presence of NEt_3 . Oxidation using X_2 leads to Pt(III) half-lanterns $[\text{Pt}_2(\mu\text{-L})_2(\text{bzq})_2(\text{X})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) having a covalent Pt–Pt bond. Alternatively, the $S^{\wedge}N$ ligands 2-mercaptobenzothiazolate and 2-mercaptobenzoxazolate have been used to prepare the corresponding complexes. The short Pt··Pt contacts of about 3 Å in the Pt(II) complexes provide interesting optical properties. Oxidation using X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) yields the diamagnetic binuclear Pt(III) complexes with Pt–Pt distances of about 2.6 Å.

Instead of short Pt(II)··Pt(II) contacts as in the half-lantern complexes, a real Pt(I)–Pt(I) bond of only 2.8209(2) Å (XRD) provides the basis for a long-lived, orange emission of the binuclear complex $[(\text{PHCy}_2)(\text{Me}_3\text{SiC}\equiv\text{C})\text{Pt}(\mu\text{-PCy}_2)(\mu\text{-H})\text{Pt}(\text{PHCy}_2)\{\kappa^2\text{P-O-}\mu\text{-P}(\text{O})\text{Cy}_2\}]$ reported by Piero Mastroilli and coworkers [18]. The emission, which is observed in the solid state at 77 K, originates from a metal-metal to ligand charge transfer (MMLCT) ($\text{L} = \text{alkynyl}$) excited state. This complex contains a bridging hydride and was obtained through protonation of the Pt(I)–Pt(I) bond in the phosphinito phosphanido precursor complex $[(\text{PHCy}_2)\text{Pt}(\mu\text{-PCy}_2)\{\kappa^2\text{P, O-}\mu\text{-P}(\text{O})\text{Cy}_2\}\text{Pt}(\text{PHCy}_2)]$.

Another type of interesting luminescent material is reported in the paper by Elena Lalinde, Maria Teresa Moreno and coworkers [19]. The here reported, binuclear $[\{\text{Pt}(\text{pq})(\text{C}\equiv\text{C}^t\text{Bu})\}_2(\mu\text{-L})]$ and trinuclear $[\{\text{Pt}(\text{pq})(\text{C}\equiv\text{C}^t\text{Bu})\}_3(\mu\text{-L})]$ ($\text{L} = \mu\text{-1,3,5-tris(pyridine-4-ylethynyl)benzene}$; Hpq = phenylquinoline) complexes were formed by bridge-splitting reactions with $[\text{Pt}(\text{pq})(\mu\text{-}\kappa\text{C}\alpha:\eta^2\text{-C}\equiv\text{C}^t\text{Bu})_2]$. The complexes are characterized by a combination of ^1H NMR spectroscopy, mass spectrometry and XRD. ^1H NMR proves the existence of a dynamic equilibrium in solution between the diplatinum complexes, the corresponding mononuclear complex with terminal N -donor ligands, the starting material and the free ligand (L) and the effects of concentration, temperature and solvent properties on the equilibrium have been studied. The complexes exhibit a broad absorption range ($\lambda < 500$ nm), are strong emitters, with maxima around 600 nm, and the corresponding excited states show contributions from pq, L, $\text{C}\equiv\text{C}^t\text{Bu}$ and the metal as analyzed by TD-DFT calculations.

The new cyclometalated Pt complexes containing pyridine-functionalized coumarin ligands and acetylacetonate reported by Rainer F. Winter and coworkers are revealed to be rather strong triplet emitters and, thus, suitable for technical application [20]. The Pt atom in these two complexes is C-coordinated either to the phenyl core of coumarin (2*H*-chromen-2-one) or to the “olefinic” 4-position core, respectively. Both complexes show intense green emissions from largely coumarin-centered triplet states. Spectroelectrochemistry and quantum chemical calculations support this assignment. In the crystal structures of both complexes, multiple and strong intermolecular interactions, such as π -stacking, short Pt··Pt or C–H··O hydrogen bonding were observed.

While all the above-described Pt(II) complexes exhibit the most abundant coordination number four and a square planar geometry, higher coordinated organoplatinum(II) complexes are known and it is established that such species, especially those carrying olefin ligands, play an important role in organoplatinum catalysis. The last report presents the crystal and molecular structure of the five coordinate organoplatinum diolefin complex $[\text{Pt}(\text{bpy})(\text{cod})(\text{Me})][\text{SbF}_6]$ (cod = 1,5-cyclooctadiene, bpy = 2,2'-bipyridine) [21]. Detailed NMR spectroscopy revealed that the trigonal bipyramidal structure found in the crystal is retained in solution. Interestingly, the application of the well-established τ values for the discrimination between trigonal bipyramidal vs. square pyramidal coordination fails, which can be explained from the steric strain from the two chelate ligands. Additionally, a brief review is provided for the occurrence of further five coordinate olefin Pt(II) complexes and their importance in organocatalysis.

References

1. Nyholm, R.S. Synthesis, Structure and Reactions of Chelate Metal-Olefin Complexes. *Pure Appl. Chem.* **1971**, *27*, 127–144.
2. 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).
3. Birnbaum, K. Ueber die Einwirkung der schwefligen Säure auf Platinchlorid. *Ann. Chem. Pharm.* **1869**, *152*, 137–147 (In Germany).
4. Black, M.; Mais, R.H.B.; Owston, P.G. The Crystal and Molecular Structure of Zeise's Salt, $\text{KPtCl}_3 \cdot \text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}$. *Acta Crystallogr. B* **1969**, *25*, 1753–1759.
5. Love, R.A.; Koetzle, T.F.; Bau, R. Neutron Diffraction Study of the Structure of Zeise's Salt, $\text{KPtCl}_3(\text{C}_2\text{H}_4) \cdot \text{H}_2\text{O}$. *Inorg. Chem.* **1975**, *14*, 2653–2657.
6. Hunt, L.B. The First Organometallic Compounds. William Christopher Zeise and his Platinum Complex. *Plat. Met. Rev.* **1984**, *28*, 76–83.
7. Chock, P.B.; Halpern, J.; Paulik, F.E.; Shupack, S.I.; DeAngelis, T.P. Potassium trichloro(ethene)platinate(II) (Zeise's Salt). *Inorg. Synth.* **1990**, *28*, 349–351.
8. 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*- $[\text{PtCl}_2(\text{OH})(\eta^2\text{-C}_2\text{H}_4)]^-$ and *trans*- $[\text{PtCl}_2(\eta^1\text{-CH}_2\text{NO}_2)(\eta^2\text{-C}_2\text{H}_4)]^-$. *Dalton Trans.* **2012**, *41*, 3014–3021.
9. Pope, W.J.; Peachey, S.J. The Alkyl Compounds of Platinum. *J. Chem. Soc. Trans.* **1909**, *95*, 571–576.
10. Rundle, R.E.; Sturdivant, J.H. The Crystal Structures of Trimethylplatinum Chloride and Tetramethylplatinum. *J. Am. Chem. Soc.* **1947**, *69*, 1561–1567.

11. Ebert, K.H.; Massa, W.; Donath, H.; Lorberth, J.; Seo, B.-S.; Herdtweck, E. Organoplatinum compounds: VI. Trimethylplatinum thiomethylate and trimethylplatinum iodide. The crystal structures of $[(\text{CH}_3)_3\text{PtS}(\text{CH}_3)]_4$ and $[(\text{CH}_3)_3\text{PtI}]_4 \cdot 0.5\text{CH}_3\text{I}$. *J. Organomet. Chem.* **1998**, *559*, 203–207.
12. Kavakli, C.; Gabrielsson, A.; Sieger, M.; Schwederski, B.; Niemeyer, M.; Kaim, W. Reversible radical complex formation of an organometallic diplatinum(IV) compound. *J. Organomet. Chem.* **2007**, *692*, 3151–3155.
13. Song, A.-R.; Hwang, I.-C.; Ha, K. Tetra- μ_3 -bromido-tetrakis[trimethylplatinum(IV)]. *Acta Cryst.* **2007**, *E63*, m2259.
14. Nyholm, R.S. Electron Configuration and Structure of Transition-Metal Complexes (Tilden Lecture). *Proc. Chem. Soc. (London)* **1961**, 273–296.
15. Crespo, M. Diarylplatinum(II) Compounds as Versatile Metallating Agents in the Synthesis of Cyclometallated Platinum Compounds with N-Donor Ligands. *Inorganics* **2014**, *2*, 115–131; doi:10.3390/inorganics2010115.
16. López, C.; Bosque, R.; Pujol, M.; Simó, J.; Sevilla, E.; Font-Bardía, M.; Messeguer, R.; Calvis, C. Experimental and Theoretical Studies of the Factors Affecting the Cycloplatination of the Chiral Ferrocenylaldimine (*S*_C)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{H})=\text{N-CH}(\text{Me})(\text{C}_6\text{H}_5)\}]$. *Inorganics* **2014**, *2*, 620–648; doi:10.3390/inorganics2040620.
17. Sicilia, V.; Borja, P.; Martín, A. Half-Lantern Pt(II) and Pt(III) Complexes. New Cyclometalated Platinum Derivatives. *Inorganics* **2014**, *2*, 508–523; doi:10.3390/inorganics2030508.
18. Latronico, M.; Gallo, V.; Lalinde, E.; Ruiz, S.; Todisco, S.; Mastroilli, P. A Hydrido η^1 -Alkynyl Diplatinum Complex Obtained from a Phosphinito Phosphanido Complex and Trimethylsilylacetylene. *Inorganics* **2014**, *2*, 591–605; doi:10.3390/inorganics2040591.
19. Lalinde, E.; Moreno, M.; Ruiz, S.; Sánchez, S. Attachment of Luminescent Neutral “Pt(pq)(C \equiv CtBu)” Units to Di and Tri N-Donor Connecting Ligands: Solution Behavior and Photophysical Properties. *Inorganics* **2014**, *2*, 565–590; doi:10.3390/inorganics2040565
20. Jackel, A.; Linseis, M.; Häge, C.; Winter, R.F., Turning-On of Coumarin Phosphorescence in Pt(acac) Complexes of Cyclometalated Pyridyl-Substituted Coumarins. *Inorganics* **2015**, *3*, 55–81.
21. Klein, A.; Neugebauer, M.; Krest, A.; Lüning, A.; Garbe, S.; Arefyeva, N.; Schlörer, N. Five coordinate Platinum(II) in [Pt(bpy)(cod)(Me)][SbF₆][−]—A Structural and Spectroscopic Study. *Inorganics* **2015**, *2*, 118–138; doi:10.3390/inorganics3020118.