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Reactions of the organoplatinum complex [Pt(cod)(neoSi)Cl] (neoSi = trimethylsilylmethyl) with the non-coordinating anions SbF_6^- and BPh_4^-

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Abstract: Reactions of the organoplatinum complex [Pt(cod)(neoSi)Cl] (neoSi = (trimethylsilylmethyl) with the Ag(I) salts of oxo or fluoride containing anions $\text{A}^- = \text{NO}_3^-$, ClO_4^- , OTf^- (trifluoromethanesulfonate) and SbF_6^- lead to the desired abstraction of the chlorido ligand and precipitation of AgCl. However, further reaction of the resulting Pt complexes [Pt(cod)(neoSi)(solvent)]⁺ with diverse N-heterocyclic ligands L such as pyridines, caffeine, and guanine did not yield the targeted complexes [Pt(cod)(neoSi)(L)](A) in most of the cases, but to extensive decomposition yielding [Pt(cod)(Me)(solvent)]⁺, thus transforming the neoSi into a methyl ligand. A detailed study on the reaction with SbF_6^- combining DFT calculations with NMR and MS revealed that Pt catalysed decomposition of SbF_6^- and fluorination of the neoSi silicon atom leading to FSiMe_3 . When reacting the parent complex with Ag(BPh₄), the arylated derivative [Pt(cod)(neoSi)(Ph)] was obtained and characterised by multinuclear NMR, MS and single crystal XRD.

Keywords: neosilyl ligand; non-coordinating anions; transmetalation; fluorine; DFT calculations.

1 Introduction

Organoplatinum(II) complexes [Pt(cod)(R)(L)] (R = alkyl, alkynyl or aryl; L = other ligands) with cod (1,5-cyclooctadiene) as an easily exchangeable ligand, have been known for decades and are used as precursors for mono- and polynuclear organometallic platinum(II) [1–18] compounds with applications in the field of catalysis [19–23], or chemical vapour deposition (CVD) of platinum and preparation of Pt nanoparticles [24–29]. Furthermore, following an early report by Komiya et al. [30] we and others have explored the anti-proliferative properties of complexes of the type [Pt(cod)(R)(L)] in the last years [31–37]. Thus, we could establish that the organometallic ligand R is a requirement for cell-toxicity, while the co-ligands L are less important. While the organometallic platinum(II) complexes [Pt(cod)(Me)Cl] and [Pt(cod)(Me)(Cyt)](SbF_6^-) (Cyt = cytosine) exhibit high toxicity against HT-29 and MCF-7 cancer cell lines, [Pt(cod)Cl₂] is virtually non-toxic [35,36]. The alkynyl derivative [Pt(cod)(Me)(C≡C(4Me)Ph)] exhibits IC₅₀ values of 0.2(±0.1) μM and 0.3(±0.1) μM, respectively [34] for HT-29 and MCF-7 cancer cell lines. Superior toxicity of organometallic complexes over non-organometallic derivatives has been concluded earlier from Komiya's work [30] and reports by Deacon et al. [2,38,39] who has also coined the term “rule-breakers” to point out that these compounds do not conform to the structure-activity relationships established for classical cisplatin-like Pt-containing drugs [40–42]. This makes them very interesting for the treatment of cisplatin-resistant cancers [2,40–42]. Trying to clarify the crucial role of the organometallic R ligand we also studied the reactivity of these organometallic complexes and found that the M–R bond is generally rather stable under physiological conditions for many hours even for very strongly σ-donating ligands such as methyl, neopentyl (2,2-dimethylpropyl = neop), neosilyl (trimethylsilylmethyl = neoSi), neophyl (2-methyl-2-phenylpropyl = neoPh), and benzyl (Bn) [32,35,36]. At the same time the mixed-ligand complexes [Pt(cod)(C≡CR')(Me)] undergo self-transmetalation

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R = anionic ligands, e.g. alkyl, aryl, alkynyl, thiolates, amides ...

L = neutral ligands, e.g. phosphines, amines, pyridines, nucleobases ...

Scheme 1: Frequently applied exchange of chlorido ligands in Pt(II)(cod) complexes through abstraction using Ag^+ salts.

yielding the homoleptic complexes $[Pt(cod)(C\equiv CR')_2]$ and $[Pt(cod)(Me)_2]$ which slowly decompose into R–R coupling products, cod and metallic Pt from reductive eliminations within days [34].

A broadly applied reaction to obtain new Pt(II) anti-cancer drugs from simpler chlorido Pt(II) precursors [43] is exemplified on Pt(cod) complexes in Scheme 1 [31,32,34-37,43].

In continuation of the above described project on anti-proliferative organo Pt(II) complexes we intended to transform the precursor complex $[Pt(cod)(neoSi)Cl]$ (neoSi = (trimethylsilylmethyl) into the corresponding compounds $[Pt(cod)(neoSi)(L)]A$ (L = neutral ligands such as nucleobases, pyridines; A = anion). Besides the formation of small amounts of the desired complexes, we observed some very interesting side-reactions. The neoSi ligands reacts with $Ag(SbF_6)$ in a complex cascade of reactions finally allowing to detect Me_3SiF and the aquo Pt(II) complex $[Pt(cod)(Me)(H_2O)]^+$. Also, the oxo anions of $Ag(NO_3)$ and $Ag(ClO_4)$ decompose the neoSi ligand probably forming O–SiMe₃ species. Furthermore, $[Pt(cod)(neoSi)Cl]$ is arylated in a reaction with $Ag(BPh_4)$ yielding $[Pt(cod)(neoSi)(Ph)]$. The reactions and their products were characterised using multinuclear NMR spectroscopy, MS and single crystal XRD, mechanistic details of the reactions decomposing the neoSi ligand were studied by density functional (DFT) calculations.

2 Experimental Section

2.1 Instrumentation

The NMR spectra were recorded on a Bruker Avance II 300 MHz (1H : 300.13 MHz, ^{13}C : 75.47 MHz) / Bruker Avance 400 spectrometer (1H : 400.13 MHz, ^{13}C : 100.61 MHz, ^{195}Pt : 86.01 MHz) using a triple resonance $^1H, ^{19}F, BB$ inverse probehead or on a Bruker Avance II 600 spectrometer (1H : 600.13 MHz) (Bruker, Rheinfelden, Germany). The broad

band 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 1H . The unambiguous assignment of the 1H , ^{13}C and ^{195}Pt resonances was obtained from 1H TOCSY, 1H COSY, 1H NOESY, gradient selected 1H , ^{13}C HSQC and HMBC and gradient selected 1H , ^{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 1H and ^{13}C , $Na_2[PtCl_6]$ in D_2O for ^{195}Pt and $CFCl_3$ for ^{19}F . The spectra analyses were performed by the Bruker TopSpin 1.3 software. EI-MS spectra (positive) were measured using a Finnigan MAT 900 S (MasCom, Bremen, Germany). Elemental analyses were carried out on Hekatech CHNS EuroEA 3000 Analyzer (Hekatech GmbH, Wegberg, Germany).

2.2 Crystal structure solution and refinement

The data collection on $[Pt(cod)(neoSi)(Ph)]$ was performed at $T = 293(2)$ K on a IPDSII diffractometer (STOE & Cie GmbH Darmstadt, Germany) with Mo-K α radiation ($\lambda = 0.71073$ Å) employing ω -2 θ scan technique. The structure was solved by direct methods using SIR 2014 [44] in the orthorhombic space group $Pna2_1$ (No. 33) with reasonable R values (<0.045) and low residual electron density (<1 e Å⁻³) using conventional alternating least squares methods with SHELXL-2018/3 [45] within WinGX-2014.1 [46]. Details were provided in Table S1 in the Supporting Information. All non-hydrogen atoms were treated anisotropically; hydrogen atoms were included by using appropriate riding models. CCDC 1845791 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 UK. Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk.

2.3 Quantum chemical calculations

All DFT calculations were performed with the Gaussian 09 Rev. D.01 package [47] using the B3LYP hybrid functional [48] and the SDD basis set, which consists of the D95 full double zeta basis set [49] and effective core potentials (ECP) [50] for atoms heavier than Argon. The standard convergence criteria for geometry optimisations and single point calculations were used. To include solvent effects into the calculations, the polarisable continuum model (PCM) [51,52] was used and the cavity for the molecule was formed based on the UFF model for atomic radii [53]. The local spin density approximation (LSDA) was employed for all potential scans along bond dissociation paths.

2.4 Syntheses - General

All preparations were carried out in a dry argon atmosphere using Schlenk techniques. Solvents (CH_2Cl_2 , THF, toluene, diethyl ether and MeCN) were dried using a MBRAUN MB SPS-800 solvent purification system.

2.5 Reagents

The complexes $[\text{Pt}(\text{cod})\text{Cl}_2]$ [10,35] and $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ [35,54] were prepared according to published procedures. $\text{Ag}(\text{BPh}_4)$ was prepared from $\text{Na}(\text{BPh}_4)$ and $\text{Ag}(\text{NO}_3)$ following literature procedures [55,56]. All other chemicals were purchased by commercial suppliers and were used without further purification.

2.6 Syntheses

Reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{NO}_3)$ in the presence of caffeine. In a 100 mL Schlenk flask 200 mg (0.469 mmol) $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ were dissolved in 40 mL of methanol and 79.7 mg (0.469 mmol) of $\text{Ag}(\text{NO}_3)$ were added. The mixture was stirred for 30 min and the colourless precipitate was filtered off. 91.2 mg (0.469 mmol) of caffeine were added to the filtrate the mixture was stirred for 30 min and then evaporated to dryness. The colourless residue was recrystallised from $\text{CH}_2\text{Cl}_2/n$ -pentane (1/3). Yield 165 mg (0.255 mmol; 54%) $[\text{Pt}(\text{cod})(\text{neoSi})(\text{caf})](\text{NO}_3)$. Elemental analysis found (calc.) for $\text{C}_{20}\text{H}_{33}\text{N}_5\text{O}_5\text{PtSi}$ (446.68): C 37.15 (37.14), H 5.17 (5.14), N 10.90 (10.83)%. ^1H NMR (300.13 MHz, acetone- d_6): δ = 8.10 (m, 1H, $\text{H}_{8_{\text{caf}}}$), 5.53 (m, 2H, $^2J_{\text{Pt-H}} = 36$ Hz, $\text{H}_{5,6_{\text{cod}}}$), 4.73 (m, 2H, $^2J_{\text{Pt-H}} = 84$ Hz, $\text{H}_{1,2_{\text{cod}}}$), 4.04 (s, 3H, $^1J_{\text{C-H}} = 143$ Hz, Me_{cafN7})

3.63 (s, 3H, Me_{cafN3}), 3.39 (s, 3H, Me_{cafN1}), 2.71-2.24 (m, 8H, $\text{H}_{3,4,7,8_{\text{cod}}}$), 0.75 (s, 2H, $^2J_{\text{Pt-H}} = 67$ Hz, $\text{CH}_{2_{\text{neoSi}}}$), 0.07 (s, 9H, Me_3Si) ppm.

Reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{NO}_3)$ and pyridine. An amount of 137 mg (0.321 mmol) $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ was dissolved in 15 mL of acetone and 54 mg (0.317 mmol) of $\text{Ag}(\text{NO}_3)$ were added. After stirring for 2 h the colourless precipitate was filtered off and 27 μL (0.32 mmol) pyridine was added to the filtrate. After stirring for 10 min the reaction mixture was evaporated to dryness leaving 102.3 mg of yellow sticky oil. Recrystallisation from $\text{CH}_2\text{Cl}_2/n$ -pentane (1/1) gave 45 mg of an off-white material. Yield 45 mg (0.084 mmol, 26%) $[\text{Pt}(\text{cod})(\text{neoSi})(\text{Py})](\text{NO}_3)$. Elemental analysis found (calc.) for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_3\text{PtSi}$ (531.59): C 38.15 (38.41), H 5.27 (5.31), N 5.23 (5.27)%. ^1H NMR (300.13 MHz, acetone- d_6): δ = 9.07 (m, 2H, $\text{H}_{2,6_{\text{py}}}$), 8.21 (t, 1H, $^3J_{\text{H}_{3,5-\text{H}_4}} = 7.72$ Hz, $^4J_{\text{H}_{2,6-\text{H}_4}} = 1.41$ Hz, $\text{H}_{4_{\text{py}}}$), 7.84 (dd, 2H, $^3J_{\text{H}_{3,5-\text{H}_{2,6}}} = 6.6$ Hz, $\text{H}_{3,5_{\text{py}}}$), 5.43 (m, 2H, $^2J_{\text{Pt-H}} = 27$ Hz, $\text{H}_{5,6_{\text{cod}}}$), 5.23 (m, 2H, $^2J_{\text{Pt-H}} = 76.0$ Hz, $\text{H}_{1,2_{\text{cod}}}$), 2.78-2.32 (m, 8H, $\text{H}_{3,4,7,8_{\text{cod}}}$), 0.98 (s, 2H, $^2J_{\text{Pt-H}} = 74.5$ Hz, $\text{CH}_{2_{\text{neoSi}}}$), -0.13 (m, 9H, Me_3Si). ^{195}Pt (64.52 MHz, acetone- d_6): δ = -3580(3) ppm. Remarkably, the signal was not detected in the ^{195}Pt - ^1H HMBC (64.52/300.13 MHz) experiment but was determined from the DECP90 pulse sequence. EI-MS: m/z = 469 $[\text{Pt}(\text{cod})(\text{neoSi})(\text{Py})]^+$, 390 $[\text{Pt}(\text{cod})(\text{neoSi})]^+$.

Reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{SbF}_6)$ and pyridine. 110.8 mg (0.2 mmol) of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ were dissolved in 15 mL of methanol and 68.7 mg (0.2 mmol) $\text{Ag}(\text{SbF}_6)$ were added. After stirring for 30 min the formed precipitate was filtered off and 16 μL (0.2 mmol) of pyridine were added to the filtrate. After 30 min stirring all volatiles were removed and the colourless residue was washed with n -pentane. Careful NMR analyses of this material showed that it contained at least the three complexes $[\text{Pt}(\text{cod})(\text{Me})(\text{Py})]^+$, $[\text{Pt}(\text{cod})(\text{Me})(\text{H}_2\text{O})]^+$, and $[\text{Pt}(\text{cod})(\text{neoSi})_2]$ and SbF_6^- . **$[\text{Pt}(\text{cod})(\text{Me})(\text{Py})]^+$** ^1H NMR (300.13 MHz, acetone- d_6): δ = 8.97 (m, 2H, $\text{H}_{2,6_{\text{py}}}$), 8.30 (t, 1H, $^3J_{\text{H}_{3,5-\text{H}_4}} = 7.85$ Hz, $\text{H}_{4_{\text{py}}}$), 7.90 (dd, 2H, $^3J_{\text{H}_{3,5-\text{H}_{2,6}}} = 6.8$ Hz, $\text{H}_{3,5_{\text{py}}}$), 5.50 (m, 2H, $^2J_{\text{Pt-H}} = 32$ Hz, $\text{H}_{5,6_{\text{cod}}}$), 4.82 (m, 2H, $^2J_{\text{Pt-H}} = 73$ Hz, $\text{H}_{1,2_{\text{cod}}}$), 2.8-2.5 (m, 8H, $\text{H}_{3,4,7,8_{\text{cod}}}$), 0.87 (s, 3H, $^2J_{\text{Pt-H}} = 64$ Hz, $\text{H}_3\text{C-Pt}$) ppm. **$[\text{Pt}(\text{cod})(\text{Me})(\text{H}_2\text{O})]^+$** ^1H NMR (300.13 MHz, acetone- d_6): δ = 5.71 (m, 2H, $\text{H}_{2,\text{Oligand}}$), 5.65 (m, 2H, $^2J_{\text{Pt-H}} = 35$ Hz, $\text{H}_{5,6_{\text{cod}}}$), 4.93 (m, 2H, $^2J_{\text{Pt-H}} = 91$ Hz, $\text{H}_{1,2_{\text{cod}}}$), 2.7-2.3 (m, 8H, $\text{H}_{3,4,7,8_{\text{cod}}}$), 0.88 (s, 3H, $^2J_{\text{Pt-H}} = 66$ Hz, $\text{H}_3\text{C-Pt}$) ppm. **$[\text{Pt}(\text{cod})(\text{neoSi})_2]$** ^1H NMR (300.13 MHz, acetone- d_6): δ = 4.73 (m, 4H, $^2J_{\text{Pt-H}} = 43$ Hz, $\text{H}_{1,2,5,6_{\text{cod}}}$), 4.93 (m, 2H, $^2J_{\text{Pt-H}} = 91$ Hz, $\text{H}_{1,2_{\text{cod}}}$), 2.7-2.3 (m, 8H, $\text{H}_{3,4,7,8_{\text{cod}}}$), 0.88 (s, 3H, $^2J_{\text{Pt-H}} = 66$ Hz, $\text{H}_3\text{C-Pt}$) ppm. **SbF_6^-** ^{19}F NMR (282.40 MHz, acetone- d_6) δ = -123.14 (m, 6F, $^1J_{121\text{Sb-F}} = 1939$ Hz, $^1J_{123\text{Sb-F}} = 1050$ Hz) ppm. EI-MS analysis of this material gave: m/z = 477 $[\text{Pt}(\text{cod})(\text{neoSi})]^+$, 397 $[\text{Pt}(\text{cod})(\text{Me})(\text{Py})]^+$, 390 $[\text{Pt}(\text{cod})]$

(neoSi)]⁺, 336 [Pt(cod)(Me)(H₂O)]⁺, 318 [Pt(cod)(Me)]⁺, 303 [Pt(cod)]⁺.

Reaction of [Pt(cod)(neoSi)Cl] with Ag(SbF₆). The reaction was carried out as described above with the difference that no pyridine was added. The main product from NMR analysis was [Pt(cod)(Me)(H₂O)]⁺. EI-MS analysis of the reaction mixture prior to evaporation gave signals for [SbF₆]⁺ at *m/z* = 218(75%) and 216(100%) and for FSiMe₃ at *m/z* = 92(100%) in addition to the Pt species [Pt(cod)(neoSi)]⁺ (*m/z* = 390), [Pt(cod)(Me)(H₂O)]⁺ (336), and [Pt(cod)(Me)]⁺ (318).

Reaction of [Pt(cod)(neoSi)Cl] with Ag(BPh₄) and pyridine. An amount of 66.4 mg (0.39 mmol) Ag(NO₃) was dissolved in 3 mL water. Then we added 133.5 mg (0.39 mmol) Na(BPh₄) dissolved in 6 mL water slowly to this solution whereupon a colourless gel-like precipitate formed. After centrifugation at 3000 rpm for 5 min the cloudy liquid phase was removed. 5 mL of water were added to the residue, which was washed with water (mixing + centrifugation). The thus obtained solid was suspended in MeCN and the suspension transferred to a Schlenk flask and subsequently dried. The thus purified Ag(BPh₄) was dissolved in 20 mL of MeCN and 151 mg (0.355 mmol) [Pt(cod)(neoSi)Cl] dissolved in 15 mL MeCN, were added. After stirring for 20 h at ambient temperature the formed precipitate was removed by careful filtration and 32 µL (0.39 mmol) of pyridine were added to the filtrate. After stirring for 30 min all volatiles were removed *in vacuo* and the resulting colourless solid was dissolved in MeCN and stored at -25 °C in the fridge. Yield 83 mg of colourless crystals (0.18 mmol, 50%) [Pt(cod)(neoSi)(Ph)]. A further crop of material was obtained by slowly adding *n*-heptane to the mother liquor thus precipitating 66 mg (0.14 mmol, 40%) Elemental analysis found (calc.) for C₁₈H₂₈PtSi₁ (467.58): C 46.15 (46.24), H 6.07 (6.04) %. ¹H NMR (300.13 MHz, acetone-d₆): δ = 7.25 (dd, 2H, ³J_{Pt-H} = 65.7 Hz, ³J_{H3,5-H2,6} = 8 Hz, ⁴J_{H4-H2,6} = 1.4 Hz, H2,6_{Ph}), 7.00 (dd, 2H, ³J_{H4-H3,5} = 7.4 Hz, H3,5_{Ph}) 6.82 (tt, 1H, H4_{Ph}), 5.16 (m, 2H, ²J_{Pt-H} = 39.1 Hz, H1,2_{cod}), 4.67 (m, 2H, ²J_{Pt-H} = 41.4 Hz, H5,6_{cod}), 2.53-2.40 (m, 8H, H3,4,7,8_{cod}), 0.85 (s, ²J_{Pt-H} = 99 Hz, ²J_{Si-H} = 7.5 Hz, CH_{2neoSi}), -0.26 (s, ¹J_{C-H} = 117.8 Hz, ²J_{Si-H} = 6.42 Hz, ³J_{Pt-H} = 2.4 Hz, H₃C_{neoSi}) ppm. ¹⁹⁵Pt-¹H HMBC (64.52/300.13 MHz, acetone-d₆): δ = -3542 ppm. ¹³C-NMR (75.47 MHz, acetone-d₆): δ = 156 (¹J_{Pt-C} = 1077 Hz, C1_{Ph}), 135 (²J_{Pt-C} = 33.3 Hz, C2,6_{Ph}), 127 (³J_{Pt-C} = 74.4 Hz, C3,5_{Ph}), 122 (⁴J_{Pt-C} = 12.8 Hz, C4_{Ph}), 103 (¹J_{Pt-C} = 48.7 Hz, C1,2_{cod}), 100 (¹J_{Pt-C} = 62.2 Hz, C5,6_{cod}), 29 (C3,4,7,8_{cod}), 16.6 (¹J_{Pt-C} = 720 Hz, CH_{2neoSi}), 1.6 (³J_{Pt-C} = 30.8 Hz, C₃Me_{neoSi}) ppm. EI-MS: *m/z* = 467 [Pt(cod)(neoSi)(Ph)]⁺, 390 [Pt(cod)(neoSi)]⁺, 380 [Pt(cod)(Ph)]⁺.

A small scale reaction using 50 mg (0.12 mmol) of [Pt(cod)(neoSi)Cl] and 51 mg (0.12 mmol) of freshly prepared Ag(BPh₄) applying the same work-up and final recrystallisation from MeCN/*n*-heptane (2/1) gave 53 mg (0.11 mmol, 95%) of the product.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Reaction of [Pt(cod)(neoSi)Cl] with Ag(NO₃) and caffeine or pyridine

After stirring [Pt(cod)(neoSi)Cl] with Ag(NO₃) in methanol solution for 30 min the formed AgCl precipitate was filtered off and caffeine was added. After further stirring for 30 min evaporation of the volatiles and re-crystallisation of the residue from CH₂Cl₂/*n*-pentane gave 54% yield of [Pt(cod)(neoSi)(caffeine)](NO₃) (see Experimental Section, essential NMR data in Table 1). When repeating the experiment on a smaller scale in an NMR tube, we found decomposition of the neoSi group as concluded from the formation of further ²⁹Si NMR signals in addition to the starting complex and the target complex. MS on this sample was not conclusive.

The similar reaction using pyridine yielded a product mixture from which an NMR signal set for the target complex [Pt(cod)(neoSi)(Py)]⁺ could be detected by 2D NMR spectroscopy (Table 1) [Pt(cod)(neoSi)(Py)](NO₃) was isolated in 26% yield. The very different ¹⁹⁵Pt-¹H coupling constants of the two olefin protons ²J_{Pt,H(=CH)} (Table 1) in the two new complexes [Pt(cod)(neoSi)(L)]⁺ (L = caffeine or pyridine) reflect the Pt-ligand bond strength of a ligand *trans* to the corresponding olefin proton as has been established in previous studies [5,10,31-37,57,58].

3.2 Reactions of [Pt(cod)(neoSi)Cl] with Ag(OTf) or Ag(ClO₄)

In similar reactions using Ag(OTf) (OTf = trifluoromethanesulfonate) in the presence of pyridine or Ag(ClO₄) and 2,6-dimethyl-pyridine and 9-methyl-guanine did not yield the target complexes [Pt(cod)(neoSi)(L)](A) (A = OTf or ClO₄) but exclusively unidentifiable decomposition products.

Figure 1: 300 MHz ^1H NMR (top) and ^{13}C APT (bottom) spectra of the reaction product $[\text{Pt}(\text{cod})(\text{Me})(\text{H}_2\text{O})]^+$ in acetone- d_6 . The broad signal at 5.72 ppm represents the H_2O ligand.

3.3 Reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{SbF}_6)$ and pyridine

In a further attempt, we reacted $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{SbF}_6)$ in acetone and added pyridine. Detailed (1D, 2D) NMR analysis of the product revealed that a mixture of compounds containing at least the three complexes $[\text{Pt}(\text{cod})(\text{Me})(\text{Py})]^+$, $[\text{Pt}(\text{cod})(\text{Me})(\text{H}_2\text{O})]^+$, and $[\text{Pt}(\text{cod})(\text{neoSi})_2]$ and counter anion SbF_6^- . The first two species revealed the obvious loss of the neoSi group, while Pt bound methyl ligands were detected about 0.8 ppm (details in the Experimental Section).

3.4 Reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{SbF}_6)$

A further reaction of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ with $\text{Ag}(\text{SbF}_6)$ in the absence of pyridine was carried out and the ^1H NMR spectrum (Figure 1, top) clearly shows the recently reported aqua complex $[\text{Pt}(\text{cod})(\text{Me})(\text{H}_2\text{O})]^+$ [57] as the main product, characterised by the H_2O ligand showing a broad resonance at 5.72 ppm, the two clearly different HC=olefin signals and the singlet at 0.79 ppm for the Pt-bound CH_3 ligand (Table 1). The ^{13}C APT NMR spectrum reveals a

phase pattern corresponding to a CH_3/CH group at ca. 30 ppm (Figure 1, bottom).

We investigated the temporal course of the reaction and found that Cl^- abstraction is very rapid. After adding AgSbF_6 to a solution of $[\text{Pt}(\text{cod})(\text{neoSi})\text{Cl}]$ the AgCl precipitate can be removed by filtration after two min and the NMR shows a complete conversion to the cationic complex $[\text{Pt}(\text{cod})(\text{neoSi})(\text{solvent})]^+$ (Figures S4 and S5 in the Supporting Information, SI). The reaction transforming the neoSi ligand into a methyl ligand takes about 90 min to be completed (Figure S4). Analysis of ^1H and ^{19}F NMR spectra revealed that Me_3SiF was formed as a by-product along with quantifiable amounts of HF (details in the Experimental Section, spectra in the SI). The high formation energy of about 670 kJ/mol of a $\text{Me}_3\text{Si}-\text{F}$ bond compared with ~ 380 kJ for a $\text{Me}_3\text{Si}-\text{C}$ bond [59,60] very probably drives the overall neoSi $\rightarrow$ Me transformation. The proton finally forming the methyl ligand probably stems from the non-dried solvent acetone. Furthermore, details of the reaction can only be speculated and Scheme 2 summarises our initial ideas which we then tried to back by DFT calculations.

In a first approach we calculated the attack of a F^- anion at the Si atom of the undercoordinated $[\text{Pt}(\text{cod})(\text{neoSi})]^+$ complex (Figure 3). We found that the $\text{Si}-\text{CH}_2$ bond is

Table 1: Selected NMR data of $[\text{Pt}(\text{cod})(\text{R})(\text{L})]^{n+}$ complexes.^a

entry	R	L	n	δH (=CH) <i>trans</i> to R	$^2J_{\text{Pt,H}}$ (=CH) <i>trans</i> to R	δH (=CH) <i>trans</i> to L	$^2J_{\text{Pt,H}}$ (=CH) <i>trans</i> to L	δH CH ₂ R	$^2J_{\text{Pt,H}}$ (CH ₂ R)	δPt	ref
1	neoSi	Cl	0	5.35	38	4.59	74	0.95	76	−3456	[35]
2	neoSi	neoSi	0	4.71	41	4.71	41	0.87	94	−3568	[35]
3	neoSi	caffeine	1	5.53	36	4.73	84	0.75	67	−3538	
4	neoSi	Py	1	5.43	27	5.23	76	0.98	75	−3580	
5	Me	H ₂ O	1	5.65	35	4.90	88	0.79	66	−3465	
6	Me	Py	1	5.47	34	5.30	72	0.83	71	−3651	
7	Me	acetone	1	5.65	31	4.95	90	0.88	64	-	[10]
8	Me	Cl	0	5.51	33	4.48	76	0.89	72	-	[10]
9	Me	Me	0	4.81	41	4.81	41	0.74	82	-	[10]
10	neoSi	Ph	0	4.67	41	5.16	39	0.85	99	−3542	
11	Ph	Ph ^b	0	5.05	39	5.05	39	-	-	-	[58]

^a Measured in acetone- d_6 ; chemical shifts δ in ppm, coupling constants J in Hz. ^b Measured in CD_2Cl_2 .

Scheme 2: Possible $[\text{Pt}(\text{cod})(\text{neoSi})]^{n+}\text{SbF}_6^-$ adducts and pathways for the decomposition of the neoSi ligand in $[\text{Pt}(\text{cod})(\text{neoSi})]^+$ complexes through $[\text{SbF}_6]^-$. Experimentally observed species marked in blue.

Figure 3: DFT optimised structures of the reaction of $[\text{Pt}(\text{cod})(\text{neoSi})]^+ + \text{F}^-$ (in acetone solution).

Figure 4: DFT calculated $[\text{Pt}(\text{cod})(\text{neoSi})]^+ \cdots \text{SbF}_6^-$ adduct with $\text{Pt} \cdots \text{F} \cdots \text{Sb}$ bonding (left) and its decomposition product (right) via an intermediate state (middle) as calculated in acetone solution.

cleaved with a low activation barrier of 13 kJ/mol and the observed products Me_3SiF and the fragment $[\text{Pt}(\text{cod})(\text{CH}_2^-)]$ were formed in an exothermic process releasing 85 kJ/mol. Regarding the possible origin of the F^- anion, we can exclude the dissociation of SbF_6^- forming SbF_5 and F^- as this reaction was computed to require about 433 kJ/mol in acetone, in line with previously reported values for the gas phase of about 500 kJ/mol [61]. Thus, the following scenarios are conceivable: the SbF_6^- as whole attacks either the undercoordinated Pt atom in $[\text{Pt}(\text{cod})(\text{neoSi})]^+$ (Scheme 2A), the Si atom (Scheme 2B) or the CH_2 group of the neoSi ligand (Scheme 2C) forming three different $[\text{Pt}(\text{cod})(\text{neoSi})]^+ \cdots \text{SbF}_6^-$ adduct intermediates.

Our calculations show that SbF_6^- preferably coordinates to the Pt atom forming the stable complex $[\text{Pt}(\text{cod})(\text{neoSi})(\text{SbF}_6)]$ (Figure 4) as assumed in Scheme 2A with a binding energy of 201 kJ/mol. The optimised geometry shows a square planar surrounding for the Pt centre when taking the C=C bond centroids of the cod ligand, in line with the d^8 configuration of Pt(II) (details in Figure S1 in the SI). Unfortunately, we could not find NMR spectroscopic evidence for this species in solution. The formation of the adduct $\text{HF}_3\text{P} \cdots \text{F} \cdots \text{SbF}_5$ which looks similar to this proposed intermediate is found to be exothermic with values ranging from -50 to -63 kJ/mol depending on the method [62]. In a next step $[\text{Pt}(\text{cod})(\text{neoSi})(\text{SbF}_6)]$ cleaves a F^- which is stabilised through H bridging at the

Scheme 3: Reaction of [Pt(cod)(neoSi)Cl] with Ag(BPh₄) and pyridine.

CH₂ group (Figure 4). Then the Pt bound SbF₆[−] cleaves another F[−], which forms HF by binding to the H⁺ released by the CH₂ group, which is transformed into a CHF entity. This entire sequence is exothermic by −50 kJ/mol.

Although we do not observe this CHF entity experimentally in the final products and this sequence does not directly include the C–SiMe₃ bond splitting, we expect the HF molecule, being a strong acid to dissociate into H⁺ and F[−] thereby enabling F[−] to attack to Si and trigger Si–CH₂ bond cleavage as discussed above (Figure 3). We can conclude that SbF₆[−] can be activated through binding to Pt(II) and dissociation of Pt-bound SbF₆[−] to SbF₅, SbF₄⁺ and further might be the source of F[−] for the reaction shown in Figure 3. Indeed, in ¹⁹F NMR spectra we observed sizable amounts of HF (−157 ppm) alongside with SbF₆[−] (−123.3 ppm) and FSiMe₃ (−157.8 ppm) (Figures S4 and S5 in the SI). This reaction sequence is also in line with the fact that we did not observe SbF₅ as by-product in the NMR or MS. It should be noted that the binding of SbF₆[−] to [Pt(cod)(neoSi)]⁺ does not directly catalyse Si–CH₂ bond cleavage as comparative potential energy scans with and without SbF₆[−] have shown.

The attack of SbF₆[−] at the Si atom (Scheme 2B) was calculated in two ways: (a) by moving the SbF₆[−] ion from the stable [Pt(cod)(neoSi)(SbF₆)] adduct/complex (Figure 4, left and Figure S1 in the SI) towards the Si atom. No energy minimum was found along the F[−]–Si path down to 1.7 Å (Figure S2 in the SI). (b) by approaching the SbF₆[−] ion from the other side as shown in Scheme 2B. However, SbF₆[−] was found not to bind to Si and the optimised adduct (see Figure S3) is 80.5 kJ/mol higher in energy than the one shown on the left-hand side of Figure 4.

The idea that SbF₆[−] might attack at the CH₂ group of the neoSi ligand (Scheme 2C) could also not be confirmed by DFT calculation, very probably due to the marked stabilisation of the Pt bound [Pt(cod)(neoSi)]⁺–SbF₆[−] adduct/complex.

Finally, we assume that also the oxo anions OTf[−], ClO₄[−] and to a lesser extent NO₃[−], form corresponding adducts and undergo similar decomposition reactions. The formation of a Me₃Si–OR bond (~520 KJ/mol, R = Me,

Et) [59] might drive the reaction decomposing the neoSi ligand in a similar way as for SbF₆[−].

3.5 Reaction of [Pt(cod)(neoSi)Cl] with Ag(BPh₄) and pyridine

In order to synthesise the pyridine complex [Pt(cod)(neoSi)(pyridine)]⁺ we reacted [Pt(cod)(neoSi)Cl] with the silver salt Ag(BPh₄) which contains neither oxo nor fluoro groups (Scheme 3).

The ¹H ¹⁹⁵Pt NMR spectrum (Figure 5) of the obtained product (details in the Experimental Section) reveals the product of a transmetalation reaction, the complex [Pt(cod)(neoSi)(Ph)] with two signals for the Pt-bound =CH olefin protons with coupling constants ²J_{Pt,H(=CH)} of 39 Hz for the low-field signal at δ = 5.16 and 41 Hz at the high-field signal at δ = 4.67 (further spectra in the SI). Assuming a stronger s-donating character of the neoSi ligand compared with the Ph ligand, the first signal is assigned to the HC= group *trans* to neoSi, the latter to the =CH proton *trans* to Ph [5,32,35]. This assignment was confirmed by NOESY experiments (for a spectrum, see SI). The quite similar coupling constant ²J_{Pt,H(=CH)} (Table 1) for the olefin protons *trans* to the two different ligands neoSi and Ph is remarkable since it implies similar strength of the two ligands. Comparison with the homoleptic complexes [Pt(cod)(neoSi)₂] and [Pt(cod)(Ph)₂] (Table 1) confirms this.

Tetraphenylborate acts here as a transmetalating or phenyl transfer agent. Transmetalation of transition metal complexes by tetraarylborates has been observed before for Ru(II) [63], Rh(I) [64,65], Au(I) [66,67], Cu(I) [68], Pd(II) [69], Pt(II) [70,71], and Pt(IV) [7259] and is not unexpected in view of the broad use of arylborates as arylating agents in C–C cross coupling reactions [73,74]. Furthermore, the here presented reaction reminds of the thermal rearrangement reactions of *cis*-[Pt(L)₂(CH₂–SiMe₂–Ph)₂] (L = PMe₃, PEt₃, PMe₂Ph, PPh₂Me, PPh₃) yielding the phenyl Pt(II) complexes *cis*-[Pt(L)₂(CH₂–SiMe₂–CH₂–SiMe₂Ph)(Ph)] from an intramolecular transmetalation from the CH₂–SiMe₂(Ph) ligand as reported by Young et al. [75].

Figure 5: 300 MHz ^1H NMR and $^1\text{H}^{195}\text{Pt}$ HMBC spectra of $[\text{Pt}(\text{cod})(\text{neoSi})(\text{Ph})]$ in acetone- d_6 .

Figure 6: Left: View on the unit cell of $[\text{Pt}(\text{cod})(\text{neoSi})(\text{Ph})]$ (orthorhombic $Pna2_1$) along the crystallographic c axis. Right: Molecular structure of $[\text{Pt}(\text{cod})(\text{neoSi})(\text{Ph})]$. Atoms shown as ellipsoids at 50% probability, H atoms are omitted for clarity. Important distances and angles: $\text{Pt}(1)-\text{C}(1) = 2.000(9) \text{ \AA}$, $\text{Pt}(1)-\text{C}(10) = 2.045(9) \text{ \AA}$, $\text{Pt}(1)-\text{X}(\text{A}) = 2.105(1) \text{ \AA}$, $\text{Pt}(1)-\text{X}(\text{B}) = 2.120(1) \text{ \AA}$; $\text{X}(\text{B})-\text{Pt}(1)-\text{C}(10) = 179.7(3)^\circ$, $\text{C}(1)-\text{Pt}(1)-\text{C}(10) = 88.0(3)^\circ$, $\text{C}(1)-\text{Pt}(1)-\text{X}(\text{A}) = 178.2(2)^\circ$, $\text{X}(\text{B})-\text{Pt}(1)-\text{X}(\text{A}) = 86.1(2)^\circ$, with $\text{X}(\text{A})$ being the centroid of the $\text{C}(11)=\text{C}(12)$ bond and $\text{X}(\text{B})$ the centroid of the $\text{C}(15)=\text{C}(16)$ bond. Sum of angles around Pt = 360° .

Single crystals of [Pt(cod)(neoSi)(Ph)] were obtained from saturated MeCN solutions. The compound was crystallised in the orthorhombic space group $Pna2_1$ (No. 33) with $Z = 4$ (data in the SI). Figure 6 shows that there are no intermolecular interactions in the crystal structure.

The molecular structure reveals the expected perfect planar surrounding of the Pt atom (Figure 6) when taking the centroids of the two double bonds (X(A) for C(11)=C(12) and X(B) for C(15)=C(16)). The bonding angle Pt(1)–C(1)–Si(1) of the neoSi ligand with $116.1(4)^\circ$ is little larger than the expected 109° and the C(1)–Si(1) bond is tilted by $70.3(3)^\circ$ from the coordination plane, the phenyl plane is tilted by approx. 62° . Most of the binding parameters are very similar to those of [Pt(cod)(neoSi)Cl] [35], [Pt(cod)(Ph)₂] [76], and related Pt(cod) complexes [10,19–22,31–37].

4 Conclusions and Outlook

When reacting the organoplatinum complex [Pt(cod)(neoSi)Cl] (neoSi = (trimethylsilylmethyl) with Ag(I) salts of oxo or fluoride containing anions $A^- = NO_3^-, ClO_4^-, OTf^-$ (trifluoromethanesulfonate) and SbF_6^- the expected abstraction of the chlorido ligand and precipitation of AgCl is observed. However, further reaction of the resulting Pt complexes [Pt(cod)(neoSi)(solvent)]⁺ with various N heterocyclic ligands L such as pyridines, caffeine, guanine did not yield the targeted complexes [Pt(cod)(neoSi)(L)](A). Only the nitrates [Pt(cod)(neoSi)(caffeine)](NO₃) and [Pt(cod)(neoSi)(pyridine)](NO₃) were obtained in sizeable amounts (54 and 26% yield). In all other cases product mixtures pointing to a complete loss of the neoSi ligand was observed. When using AgSbF₆ almost complete conversion to [Pt(cod)(Me)(H₂O)]⁺ was observed and Me₃SiF was observed as by-product by NMR and MS. A detailed ¹H and ¹⁹F NMR study in combination with DFT calculations show that Cl[–] is rapidly cleaved from the parent complex [Pt(cod)(neoSi)Cl], within two min reactions are complete. Attack of F[–] at the neoSi silicon atom in the undercoordinate complex [Pt(cod)(neoSi)]⁺ yields Me₃SiF and the fragment [Pt(cod)(CH₂)]⁺ in line with the observed products. At the same time, we can exclude dissociation of SbF₆[–] forming SbF₅ and F[–] for this reaction calculated to 433 kJ/mol in acetone solution. Instead, our DFT calculations show that the nucleophilic SbF₆[–] can strongly bind to the Pt(II) centre in the undercoordinated [Pt(cod)(neoSi)]⁺ fragment forming the very stable adduct or complex [Pt(cod)(neoSi)(SbF₆)], while other [Pt(cod)(neoSi)]⁺–SbF₆[–] adducts with F–Si or F–CH₂ binding were less favoured. Through this binding

to Pt(II) SbF₆[–] is activated and cleaves F[–] leading to SbF₅, SbF₄⁺ and maybe even further which might be the source of F[–] for the main reaction. For the oxo anions NO₃[–], ClO₄[–], OTf[–] similar transformation reactions into –OSiMe₃ species can be assumed, NO₃[–] seems to have a smaller tendency to this reaction compared with ClO₄[–] and OTf[–].

In order to avoid oxo or fluoro containing anions, we reacted the parent complex with Ag(BPh₄). Here, the arylated derivative [Pt(cod)(neoSi)(Ph)] was obtained almost quantitatively from a transmetalation reaction and was characterised by multinuclear NMR, MS and single crystal XRD.

Both examples demonstrate quite nicely that the complex anions SbF₆[–] and BPh₄[–] usually considered as non-coordinating and non-reactive can be activated by Pt(II) providing “F[–]” for fluorination or “Ph[–]” for arylation reactions in very rapid reactions.

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Supporting Information (SI): Fourteen figures with DFT calculated structures, NMR spectra, crystal and molecular structures are provided together with a table collecting structural data.

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