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Oxidative Addition of Cl_2, HClO to Square-Planar Pt^{II} Complexes: Synthesis and Structural Characterization of Platinum(II) and Platinum(IV) Bis(amidate) Complexes

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New bis(amidate)platinum(II) complexes with the general formula *cis*-$[Pt(RNH_2)_2(NHCO\textit{t}Bu)_2]$ were prepared by the hydrolysis of the corresponding *cis*-$[Pt(RNH_2)_2(\textit{t}BuCN)_2]^{2+}$ complex. The bis(amidate)platinum(IV) complexes with the formula *trans,cis,cis*-$[PtCl_2(RNH_2)_2(NHCO\textit{t}Bu)_2]$ (**5**: R = H, **6**: R = Et), *trans,cis,cis*-$[PtCl(OH)(RNH_2)_2(NHCO\textit{t}Bu)_2]$ (**8**: R = H, **9**: R = Et, and **10**: 2R = 1,2-*c*Hex), and mono(amidate) complex *mer*-$[PtCl_3(DACH)(NHCO\textit{t}Bu)_2]$ (**7**, DACH = *trans*-1,2-diaminocyclohexane) have been generated selectively by the oxidative addition of Cl_2 and HClO to the corresponding platinum(II) complexes, $[Pt(RNH_2)_2(NHCO\textit{t}Bu)_2]$, in water. All the prepared compounds were characterized by elemental analyses and ^1H and ^{195}Pt NMR spectroscopy. The structures of *trans,cis,cis*-$[PtCl_2(NH_3)_2(NHCO\textit{t}Bu)_2]$ (**5**), *trans,cis,cis*-$[PtCl_2(EtNH_2)_2(NHCO\textit{t}Bu)_2]$ (**6**), *mer*-$[PtCl_3(DACH)(NHCO\textit{t}Bu)]$ (**7**), and *trans,cis,cis*-$[PtCl(OH)(DACH)(NHCO\textit{t}Bu)_2]$ (**10**) have been confirmed by X-ray diffraction analyses. The structures of these platinum(IV) complexes adopt an octahedral geometry. The Pt–N, Pt–O, and Pt–Cl distances are in the expected ranges. These complexes are rare examples of bis(amidate)- and mono(amidate)platinum(IV) complexes.

Introduction

Since the discovery of the antitumor activity of *cis*-$Pt(NH_3)_2Cl_2$ by Rosenberg and co-workers[1] a large number of platinum(II) and platinum(IV) complexes containing *cis*-$(NH_3)_2Pt$ or *cis*-$(RNH_2)_2Pt$ units have been prepared and characterized.[2,3] Numerous efforts have been made to develop new antitumor compounds that do not show cross-resistance with *cis*-platin. *cis*-$[Pt(RNH_2)_2(amidate)_2]$ complexes, derived from *cis*-$Pt(RNH_2)Cl_2$ have proved to be useful building blocks to assemble homo- and heteronuclear dimeric,[3] oligomeric,[4] and polymeric complexes.[5] The two mutually *cis* amidate ligands play a critical role in favoring the association of the platinum units and other metal ions such as in the biologically active "platinum blues".[6] The amidate-bridged dimeric platinum complex $[Pt_2(NH_3)_4(NHCO\textit{t}Bu)L_2]^{2+}$, where L is NO_3^- or solvent molecules, has been found to activate C–H bonds of ketones[7] and to catalyze the ketonation of alkynes, epoxidation, and dihydroxylation of terminal olefins.[8]

It is well known that the Pt^{IV} species are involved in the activation of C–H bonds such as the Shilov system, which consists of aqueous solutions of Pt^{II} and Pt^{IV} salts that convert alkanes to the corresponding chlorides and alcohols under mild conditions.[9] Taking into account the fascinating chemistry of bis(amidate)platinum(III) complexes, the amidatoplatinum(IV) complexes may also be useful for such types of organic transformation processes. Furthermore, although most of the platinum centered antitumor drugs are platinum(II) compounds, in recent years a number of platinum(IV) complexes have also been found to be active for antitumor treatment with improved pharmacological properties.[10] However, so far no bis(amidate)- and mono(amidate)platinum complexes having a Pt^{IV} center have been reported. Here we report for the first time the preparation, ^1H and ^{195}Pt NMR spectra, and structural characterization of the platinum(IV) complexes *mer*-$[PtCl_3(DACH)(NHCO\textit{t}Bu)]$ (DACH = *trans*-1,2-diaminocyclohexane), *trans,cis,cis*-$[PtCl_2(RNH_2)_2(NHCO\textit{t}Bu)_2]$, and *trans,cis,cis*-$[PtCl(OH)(RNH_2)_2(NHCO\textit{t}Bu)_2]$ (R = H, Et; and 2R = 1,2-cHex). These platinum(IV) complexes were prepared by oxidative addition of Cl_2 and HClO to their corresponding platinum(II) complexes, *cis*-$[Pt(RNH_2)_2(NHCO\textit{t}Bu)_2]$, in high yields.

Results and Discussion

Synthesis and NMR Characterization

The $[Pt(RNH_2)_2(NHCO\textit{t}Bu)_2]$ complexes are easily prepared in high yield by basic hydrolysis of their corresponding platinum(II)-nitrile complexes, $[Pt(RNH_2)_2(\textit{t}BuCN)_2]^{2+}$. This procedure has been employed to prepare $[Pt(NH_3)_2$-

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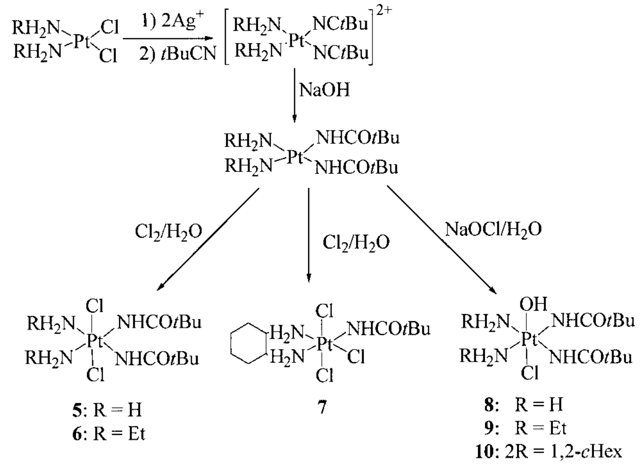
(NHCO*t*Bu)$_2$] and *cis*-[Pt(DACH)(NHCO*t*Bu)$_2$]. *cis*-[Pt(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$] and *cis*-[Pt(DACH)(NHCO*t*Bu)$_2$] were similarly obtained. The synthetic strategy for making the platinum(II) as well as platinum(IV) complexes described below is shown in Scheme 1. These platinum(II) complexes are isolated as stable colorless crystalline solids, and they are soluble in acetone, ethanol, and chloroform. The neutral square-planar complexes, *cis*-[Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$] and *cis*-[Pt(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$], react with an equimolar amount of Cl$_2$ (0.3% in water) at room temperature to give the bis(amidate)platinum(IV) complexes, *trans,cis,cis*-[PtCl$_2$(NH$_3$)$_2$(NHCO*t*Bu)$_2$] (**5**) and *trans,cis,cis*-[PtCl$_2$(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$] (**6**), as yellow crystals, respectively. However, *mer*-[PtCl$_3$(DACH)(NHCO*t*Bu)] (**7**) was generated as the sole isolated product when *cis*-[Pt(DACH)(NHCO*t*Bu)$_2$] was dissolved in Cl$_2$/H$_2$O under the same conditions. The reactions proceeded in good yields. The initially formed [PtCl$_2$(DACH)(NHCO*t*Bu)$_2$] probably further reacted with HCl to lose one molecule of *t*BuCONH$_2$ and yield the final product, **7**. The isolated crystals of **5**–**7** are poorly soluble in common organic solvents, but are moderately soluble in dimethyl sulfoxide. Their ^{195}Pt NMR spectra exhibit a singlet at –35, –30.6, and –289 ppm, respectively, indicative of typical platinum(IV) compounds.



Scheme 1.

Sodium hypochlorite has proved to be a convenient oxygen source for olefin epoxidation catalyzed by transition-metal complexes.[11] We found that it also acts as a Cl$^-$ and HO$^-$ source for the preparation of (chloro)(hydroxo)platinum(IV) complexes. The platinum(II) complexes *cis*-[Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$], *cis*-[Pt(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$], and *cis*-[Pt(DACH)(NHCO*t*Bu)$_2$] easily dissolved in an aqueous solution of NaOCl (available Cl$_2$ 5%) at room temperature and yielded *trans,cis,cis*-[PtCl(OH)(RNH$_2$)$_2$(NHCO*t*Bu)$_2$] {R = H, **8**; R = Et, **9**; (RNH$_2$)$_2$ = DACH, **10**} in moderate yields. All these chloro(hydroxo)platinum(IV) complexes were isolated as yellow solids. The ^{195}Pt NMR spectra of **8**–**10** in [D$_6$]acetone exhibit singlets at –134, –146, and 189 ppm, respectively, which are typical of Pt^{IV} species. The ^{195}Pt NMR spectrum of **10** measured immediately upon dissolving in [D$_6$]DMSO shows two singlets at 189 and –193 ppm. The downfield signal disappeared and the upfield signal was intensified after the solution stood in an NMR tube for 24 h. After this time the ^{1}H NMR spectrum also became simpler. Thus the upfield signal at δ = –193 ppm is assigned to the solvated species [Pt(OH)(DMSO)(DACH)(NHCO*t*Bu)$_2$]Cl.

The general synthetic route to platinum(IV) complexes is the oxidation of platinum(II) complexes by hydrogen peroxide or halogens.[12] The oxidative addition of HOCl with NaOCl provides a convenient route for the preparation of chloro(hydroxo)platinum(IV) complexes.

Structural Description

The structures of compounds **4**–**7** and **10** have been determined by X-ray diffraction. A summary of the crystallographic data can be found in Table 1. Colorless crystals of **4** were obtained by slow evaporation of its acetone/water solution. Compound **4** crystallizes in a chiral orthorhombic space group $P2_12_12$, and the chiral configuration is predetermined by the diamine, 1*R*,2*R*-*trans*-diaminocyclohexane. The structure of **4** established by X-ray diffraction analysis is shown in Figure 1. As expected, the central platinum is tetra-coordinated to four nitrogen atoms in a square-planar geometry. The shortness of the C–O and C–N bond lengths illustrates the sp^2 character of the related atoms. The structure of **4** is the first crystal structure of a platinum(IV) complex of the type [Pt(RNH$_2$)$_2$(*trans*-Cl$_2$)(amidate)$_2$] in which the chlorine atoms occupy the axial positions of an octahedral geometry.

Although compounds **5** and **6** crystallize in different noncentrosymmetric space groups *C*2 and *Pc*, respectively, they display the same structure. The structure of **5** is depicted in Figure 2 and the structure of compound **6** is given as Supporting Information. There are two independent molecules in the asymmetric crystallographic unit of compound **6**, which have essentially the same structure. Therefore, only one of the two molecules is shown in the Supporting Information. The coordination polyhedrons of the complexes are distorted octahedrons for both **5** and **6**. The two amine and two amidate ligands are in mutual *cis* positions, and the two chloride ions are in mutual *trans* positions. The sum of the angles of the neighboring nitrogen atoms around Pt is 359.8° for **5** and 360.5° for **6**, indicating their coplanarity. The Pt–Cl bond lengths [2.324(8) and 2.328(7) Å for **5**, 2.311(2) and 2.319(2) Å for **6**] are in good agreement with other structurally characterized platinum chloride compounds.[13] The NH$_3$ and NH$_2$ groups in **5** and **6** are involved in intra- and intermolecular hydrogen bonding. The Cl–Pt–Cl angles [179.24(8)° for **5** and 177.01(6)° for **6**] are close to 180°.

The trichloroplatinum(IV) complex **7** crystallizes in an orthorhombic space group *Pbca*. Its unit cell contains eight molecules of [PtCl$_3$(DACH)(NHCO*t*Bu)$_2$] and eight molecules of acetone. The structure of **7** consists of an octahe-

Table 1. Crystal data and structure refinement details for *trans,cis,cis*-[$PtCl_2(NH_3)_2(NHCOtBu)_2$] (**5**), *trans,cis,cis*-[$PtCl_2(EtNH_2)_2(NHCOtBu)_2$] (**6**), *mer*-[$PtCl_3$(DACH)$(NHCOtBu)_2$]·$(CH_3)_2CO$ (**7**), and *trans,cis,cis*-[PtCl(OH)(DACH)$(NHCOtBu)_2$] (**10**).

	4	**5**	**6**	**7**	**10**
Formula	$C_{16}H_{40}N_4O_5Pt$	$C_{10}H_{26}Cl_2N_4O_2Pt$	$C_{14}H_{34}Cl_2N_4O_2Pt$	$C_{14}H_{30}Cl_3N_3O_3Pt$	$C_{16}H_{39}ClN_4O_5Pt$
Formula mass	563.61	500.34	556.44	573.84	598.05
Crystal size [mm]	0.08 × 0.15 × 0.36	0.10 × 0.12 × 0.26	0.24 × 0.30 × 0.31	0.10 × 0.12 × 0.23	0.08 × 0.08 × 0.28
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_12_12$	$C2$	Pc	$Pbca$	$P2_1$
a [Å]	21.556(5)	24.181(11)	11.752(14)	18.161(4)	12.738(4)
b [Å]	25.509(6)	5.921(3)	9.939(12)	12.768(2)	20.352(6)
c [Å]	8.3333(18)	12.625(6)	18.72(2)	18.752(4)	18.372(5)
β [°]	90	106.327(8)	96.89(2)	90	90.282(6)
V [Å^3]	4582.2(17)	1734.6(14)	2171(4)	4348.3(14)	4763(2)
Z	8	4	4	8	8
ρ_{calcd} [mg/m^3]	1.634	1.916	1.702	1.937	1.668
θ range [°]	1.24–27.52	1.68–27.56	1.75–27.63	2.23–27.54	1.11–27.54
Reflections collected	26253	5387	11931	21860	28487
Reflections unique (R_{int})	10132 (0.0363)	3623 (0.0458)	8102 (0.0335)	4854 (0.0978)	18554 (0.1010)
Goodness-of-fit	1.370	1.024	1.044	1.035	0.869
R_1, wR_2 [$I > 2\sigma(I)$]	0.0718, 0.1764	0.0314, 0.0771	0.0332, 0.0873	0.0392, 0.0981	0.0678, 0.1321
R_1, wR_2 (all data)	0.0732, 0.1770	0.0344, 0.0789	0.0394, 0.0919	0.0609, 0.1085	0.1712, 0.1597
Absolute structure parameter	0.00	–0.003(11)	0.00		0.00

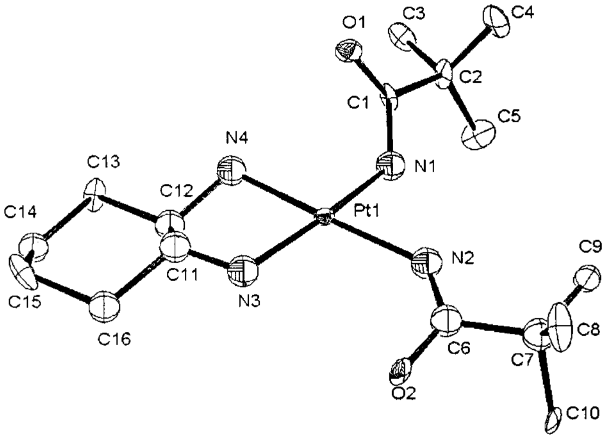


Figure 1. Molecular structure of [Pt(DACH)$(NHCOtBu)_2$] (**4**). Selected bond lengths and angles: Pt(1)–N(1) 2.055(11), Pt(1)–N(2) 2.098(15), Pt(1)–N(3) 2.062(12), Pt(1)–N(4) 2.051(15), N(4)–Pt(1)–N(1) 93.5(5), N(4)–Pt(1)–N(3) 80.6(6), N(1)–Pt(1)–N(3) 173.2(7), N(4)–Pt(1)–N(2) 178.3(6, N(1)–Pt(1)–N(2) 85.1(5 N(3)–Pt(1)–N(2) 100.9(6).

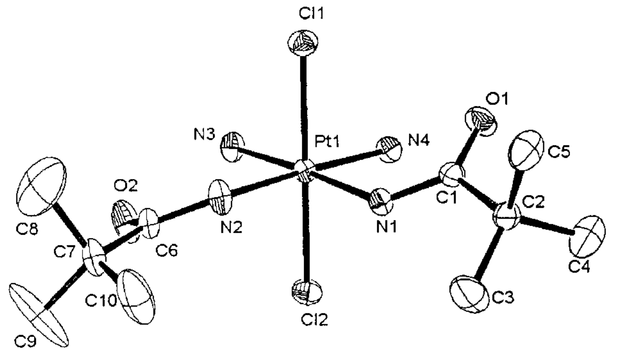


Figure 2. Molecular structure of *trans,cis,cis*-[$PtCl_2(NH_3)_2(NHCOtBu)_2$] (**5**). Selected bond lengths [Å] and angles [°]: Pt(1)–Cl(1) 2.316(2), Pt(1)–Cl(2) 2.300(2), Pt(1)–N(1) 2.016(6), Pt(1)–N(2) 1.991(7), Pt(1)–N(3) 2.070(7), Pt(1)–N(4) 2.059(6), N(2)–Pt(1)–N(1) 86.6(3), N(2)–Pt(1)–N(4) 176.8(3), N(1)–Pt(1)–N(4) 90.7(3), N(2)–Pt(1)–N(3) 92.4(3), N(1)–Pt(1)–N(3) 177.0(3), N(4)–Pt(1)–N(3) 90.1(3), N(2)–Pt(1)–Cl(2) 89.3(2), N(1)–Pt(1)–Cl(2) 87.54(19), N(4)–Pt(1)–Cl(2) 88.8(2), N(3)–Pt(1)–Cl(2) 89.6(2), N(2)–Pt(1)–Cl(1) 91.3(2), N(1)–Pt(1)–Cl(1) 93.0(2), N(4)–Pt(1)–Cl(1) 90.6(2), N(3)–Pt(1)–Cl(1) 89.9(2), Cl(2)–Pt(1)–Cl(1) 179.24(8).

drally coordinated platinum(IV) center in which the platinum atom is surrounded by three nitrogen and three chlorine atoms in a meridional fashion. The structure is depicted in Figure 3. The cyclohexyl ring exhibits pseudoplanarity as a consequence of the racemic mixture and disorder. The Pt–Cl bond lengths are not unusual, but the chlorine atom *trans* to the nitrogen atom has a rather longer Pt–Cl distance [2.329(2) Å] than the other two in mutually *trans* positions [2.311(2) and 2.319(2) Å]. However, it should be pointed out that an opposite trend has been observed in *cis*-[$PtCl_4${NH=C(Et)OMe}$_2$].[14] All other bond lengths and angles are as expected and agree perfectly with the values already reported for bis(amidate) platinum complexes.[15]

Compound **10** crystallizes in the noncentrosymmetric space group $P2_1$, and the chirality is predetermined by the ligand 1*R*,2*R*-*trans*-1,2-diaminocyclohexane. Figure 4 depicts the molecular structure of **10** with an atomic labeling scheme. The PtN_4 moiety maintains its *cis*-arrangement. The chloride and hydroxide groups are located in axial positions with normal Pt–O and Pt–Cl distances. The Pt–O distance [2.043(16) Å] is consistent with those found in other platinum hydroxide complexes,[16] and the O–Pt–Cl angle is 179.1(5)°. One of the two C=O groups is oriented toward the NH_2 group as shown in Figure 4. The N(3)···O(3) distance is 2.71 Å, indicating intramolecular hydrogen bonding.

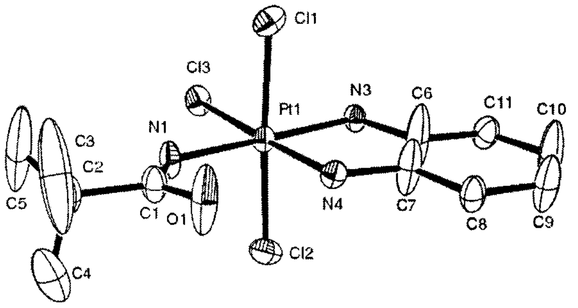


Figure 3. Molecular structure of *mer*-[$PtCl_3$(DACH)(NHCO*t*Bu)] (**7**). Selected bond lengths [Å] and angles [°]: Pt(1)–Cl(1) 2.311(2), Pt(1)–Cl(2) 2.319(2), Pt(1)–Cl(3) 2.329(2), Pt(1)–N(1) 2.009(6), Pt(1)–N(3) 2.056(5), Pt(1)–N(4) 2.051(5), N(1)–Pt(1)–N(4) 96.7(2), N(1)–Pt(1)–N(3) 179.3(3), N(4)–Pt(1)–N(3) 83.0(2), N(1)–Pt(1)–Cl(1) 91.2(2), N(4)–Pt(1)–Cl(1) 88.95(18), N(3)–Pt(1)–Cl(1) 88.21(17), N(1)–Pt(1)–Cl(2) 90.8(2), N(4)–Pt(1)–Cl(2) 87.91(18), N(3)–Pt(1)–Cl(2) 89.78(17), Cl(1)–Pt(1)–Cl(2) 176.46(7), N(1)–Pt(1)–Cl(3) 86.92(17), N(4)–Pt(1)–Cl(3) 176.38(16), N(3)–Pt(1)–Cl(3) 93.38(15), Cl(1)–Pt(1)–Cl(3) 90.57(7), Cl(2)–Pt(1)–Cl(3) 92.45(7).

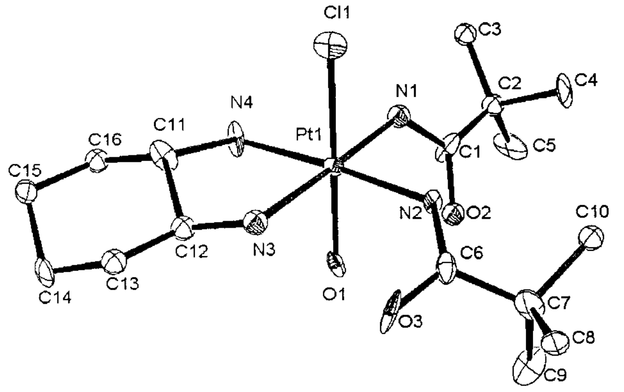


Figure 4. Molecular structure of *trans,cis,cis*-[PtCl(OH)(DACH)$(NHCOtBu)_2$] (**10**). Selected bond lengths [Å] and angles [°]: Pt(1)–N(1) 2.021(17), Pt(1)–N(2) 2.014(18), Pt(1)–N(3) 2.094(18), Pt(1)–N(4) 2.07(2), Pt(1)–Cl(1) 2.338(7), Pt(1)–O(1) 2.043(16), N(2)–Pt(1)–N(1) 87.2(8), N(1)–Pt(1)–N(4) 95.0(8), N(2)–Pt(1)–N(3) 96.0(9), N(2)–Pt(1)–N(4) 176.0(9), N(1)–Pt(1)–N(3) 176.5(8), N(4)–Pt(1)–N(3) 81.8(8), N(2)–Pt(1)–O(1) 87.1(7), N(1)–Pt(1)–O(1) 92.3(6), O(1)–Pt(1)–N(4) 89.4(7), O(1)–Pt(1)–N(3) 86.4(7), N(2)–Pt(1)–Cl(1) 93.7(6), N(1)–Pt(1)–Cl(1) 87.4(5), N(3)–Pt(1)–Cl(1) 93.8(6), N(4)–Pt(1)–Cl(1) 89.8(6), O(1)–Pt(1)–Cl(1) 179.1(5).

In summary, oxidative addition of chlorine or HOCl to the neutral [$Pt(RNH_2)_2(NHCOtBu)_2$] complexes in water yielded a number of bis(amidate) and mono(amidate) platinum(IV) complexes. Complexes **5**–**10** represent the first fully characterized examples of platinum(IV) mono(amidate) and bis(amidate) complexes derived from oxidative addition. The present study also provides a convenient synthetic route for chloro(hydroxo)platinum(IV) complexes using NaClO as the source of the chloride and hydroxide ions. Furthermore, these complexes may potentially be precursors for the preparation of some Pt^{IV} compounds since the Cl atoms can easily be replaced by other anions.

Experimental Section

General Remarks: *cis*-$Pt(EtNH_2)_2Cl_2$,[17] Pt(DACH)Cl_2 (DACH = *trans*-1,2-diaminocyclohexane),[18] *cis*-[$Pt(NH_3)_2(NHCOtBu)_2$]·$2H_2O$,[19] and *cis*-[Pt(DACH)$(NHCOtBu)_2$]·$4H_2O$[19] were prepared according to previously published procedures. Cl_2/H_2O (available chlorine 0.3 %), NaClO/H_2O (available Cl_2 5.0 %), and other chemicals were purchased from commercial sources and used as received. The elemental analyses were performed with a Perkin–Elmer PE 2400II analyzer. The ^1H and ^{195}Pt NMR spectra were recorded with a Bruker 500 MHz spectrometer. The NMR chemical shifts are given in ppm relative to TMS (^1H) and K_2PtCl_4 (^{195}Pt), and referenced either to residual solvent signals (^1H) or externally (^{195}Pt).

CAUTION! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

***cis*-[$Pt(EtNH_2)_2(NCtBu)_2$]$(ClO_4)_2$ (1):** A suspension of *cis*-$Pt(EtNH_2)_2Cl_2$ (0.36 g, 1.0 mmol) in water (10 mL) was treated with $AgClO_4$ (0.41 g, 2.0 mmol), and the mixture was stirred overnight in the dark. After the removal of AgCl, *t*BuCN (1.0 g, 12.0 mmol) was added to the filtrate. The resulting white precipitate was separated and washed with H_2O, EtOH, and Et_2O, and dried in vacuo. Yield: 0.53 g (82 %). $C_{14}H_{32}Cl_2N_4O_8Pt$ (650.41): calcd. C 25.85, H 4.96, N 8.61; found C 25.81, H 4.87, N 8.50. ^1H NMR (500 MHz, [D_6]acetone): 2.62 (q, J_{HH} = 7.0 Hz, CH_2CH_3, 4 H), 1.52 (s, $C(CH_3)_3$, 18 H), 1.10 (t, CH_2CH_3, 6 H) ppm. ^{195}Pt NMR (107.30 MHz, [D_6]acetone): δ = –2857 ppm.

***cis*-[$Pt(EtNH_2)_2(NHCOtBu)_2$]·H_2O (2):** A suspension of **1** (1.30 g, 2.0 mmol) in water (10 mL) was treated with NaOH (0.20 g, 5.0 mmol). The mixture was stirred overnight at room temperature. The resulting white solid was collected by filtration, washed with cold water and dried in vacuo. Condensing the filtrate and cooling at 5 °C afforded the second crop of the product. Yield: 0.88 g (87 %). $C_{14}H_{34}N_4O_2Pt$·H_2O (503.54): calcd. C 33.39, H 7.21, N 11.13; found C 33.29, H 7.31, N 11.12. ^1H NMR (500 MHz, [D_6]acetone): δ = 6.24 (br. s. NH_2, 4 H), 4.89 (s, NH, 2 H), 2.75 (q, J_{HH} = 6.8 Hz, CH_2, 4 H), 1.17 (t, CH_2CH_3, 6 H), 1.10 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.00 MHz, [D_6]acetone): δ = –2564 ppm.

***cis*-[Pt(1*R*,2*R*-DACH)$(NCtBu)_2$]$(ClO_4)_2$ (3):** The compound was prepared according to the procedure above for **1** using Pt(1R,2R-DACH)Cl_2 (0.38 g, 1.0 mmol) instead of *cis*-$Pt(EtNH_2)Cl_2$. Yield: 0.62 g (92 %). $C_{16}H_{32}N_4Cl_2O_8Pt$ (674.43): calcd. C 28.49, H 4.78, N 8.31; found C 28.40, H 4.92, N 8.25. ^1H NMR (500 MHz, [D_6]acetone): 1.54 (s, CH_3, 18 H), 2.75, 2.20, 1.56, 1.38, 1.20 (m, C_6H_{10}, 10 H) ppm. ^{195}Pt NMR (107.30, [D_6]acetone): –2857 ppm.

***cis*-[Pt(1*R*,2*R*-DACH)$(NHCOtBu)_2$]·$3H_2O$ (4):** The compound was prepared according to the procedure above for **2** using [Pt(1R,2R-DACH)$(NCtBu)_2$]$(ClO_4)_2$ (0.62 g, 0.09 mmol) instead of [$Pt(EtNH_2)(NCtBu)_2$]$(ClO_4)_2$. Yield: 0.48 g (94 %). $C_{16}H_{34}N_4O_2Pt$·$3H_2O$ (563.59): calcd. C 34.10, H 7.15, N 9.94; found C 34.44, H 6.74, N 9.94. ^1H NMR (500 MHz, [D_6]acetone): δ = 6.51, 4.65 (m, NH_2, each 2 H), 5.59 (s, NH, 2 H), 2.31, 1.94, 1.53, 1.35 (m, C_6H_{10}, 10 H), 1.08 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30 MHz, [D_6]acetone): δ = –2626 ppm.

***trans,cis,cis*-[$PtCl_2(NH_3)_2(NHCOtBu)_2$] (5):** [$Pt(NH_3)_2(NHCOtBu)_2$]·$2H_2O$ (47 mg, 0.10 mmol) was suspended in Cl_2/H_2O (2.36 mL, 0.3 %). The mixture was stirred for 10 min to yield a yellow solution. After the solvent was removed with a rotary evaporator, the yellow solid was washed with cold water and dried in vacuo. Crystals of **5** suitable for X-ray diffraction analysis were grown by slow evaporation of its aqueous solution. Yield: 42 mg (84%). $C_{10}H_{26}Cl_2N_4O_2Pt$ (500.32): calcd. C 24.01, H 5.24, N 11.20; found C 23.85, H 4.98, N 11.46. ^1H NMR (500 MHz, [D]DMSO): δ = 6.12 (s, NH, 2 H), 5.89 (s, NH_3, 6 H), 1.14 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt (107.00 MHz, [D]DMSO): δ = –35 ppm.

***trans,cis,cis*-[PtCl$_2$(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$]·H$_2$O (6):** The compound was prepared according to the procedure above for **5** using [Pt(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$]·H$_2$O (50.3 mg, 0.1 mmol) in place of [Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$]·2H$_2$O. Yield: 41.7 mg (75%). $C_{14}H_{34}Cl_2N_4O_2Pt$ (556.43): calcd. C 30.22, H 6.16, N 10.07; found C 30.10, H 6.25, N 9.96. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.09 (s, NH_2, 4 H), 5.63 (s, NH, 2 H), 2.64 (m, CH_2, 4 H), 1.15, 1.06 (both t, J_{HH} = 7.2 Hz, CH_2CH_3, each 3 H), 1.09 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt (107.30 MHz, [D$_6$]DMSO): δ = –31 ppm.

***mer*-[PtCl$_3$(DACH)(NHCO*t*Bu)]·(CH$_3$)$_2$CO (7):** The compound was prepared according to the procedure above for **5** using [Pt(DACH)(NHCO*t*Bu)$_2$]·3H$_2$O (67.4 mg, 0.1 mmol) instead of [Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$]·2H$_2$O. Yield: 31.7 mg, (67%). $C_{11}H_{24}Cl_3PtO$ (473.74): calcd. C 29.30, H 5.27, N 7.32; found C 29.45, H 5.29, N 7.07. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.81–6.26 (m, NH + NH_2, 5 H), 1.09, 1.53, 2.06, 2.71 (m, C_6H_{10}, 10 H), 1.12 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30 MHz, [D$_6$]-DMSO): δ = –289 ppm.

***trans,cis,cis*-[PtCl(OH)(NH$_3$)$_2$(NHCO*t*Bu)$_2$] (8):** *cis*-[Pt(NH$_3$)$_2$-(NHCO*t*Bu)$_2$]·2H$_2$O (47 mg, 0.10 mmol) was suspended in NaClO/H$_2$O (2 mL, available Cl$_2$ 5.0%). The mixture was stirred for 10 min to yield a yellow solution. After the solvent was removed with a rotary evaporator, the yellow solid was washed with cold water and dried in vacuo. Yield: 20.2 (42%). $C_{10}H_{27}ClN_4O_3Pt$ (481.88): calcd. C 24.92, H 5.65, N 11.63; found C 24.83, H 5.80, N 11.49. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 6.15 (s, NH, 2 H), 5.31, 4.82 (s, NH_3, 6 H), 1.14 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30 MHz, [D$_6$]DMSO): δ = –134 ppm.

***trans,cis,cis*-[PtCl(OH)(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$]·H$_2$O (9):** The compound was prepared according to the procedure above for **8** using [Pt(EtNH$_2$)$_2$(NHCO*t*Bu)$_2$]·H$_2$O (50.3 mg, 0.1 mmol) instead of [Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$]·2H$_2$O. Yield: 35 mg (63%). $C_{14}H_{35}ClN_4O_3Pt\cdot H_2O$ (556.00): calcd. C 30.24, H 6.71, N 10.08; found C 30.24, H 6.53, N 9.89. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 6.46 (s, NH, 2 H), 7.05, 4.92 (s, NH_2, 4 H), 2.70 (q, J_{HH} = 7.0 Hz, CH_2, 4 H), 1.15 (t, CH_2CH_3, 6 H), 1.07 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30 MHz, [D$_6$]DMSO): δ = –146 ppm.

***trans,cis,cis*-[PtCl(OH)(DACH)(NHCO*t*Bu)$_2$] (10):** A suspension of [Pt(DACH)(NHCO*t*Bu)$_2$] (52 mg, 0.1 mmol) in water was treated with an aqueous solution of NaClO (2 mL, available Cl$_2$ 5%). A yellow solution was yielded after stirring for 30 min. Yellow crystals were grown upon slow evaporation of the resulting yellow solution. Yield: 43.8 mg (78%). $C_{16}H_{35}ClN_4O_3Pt$ (562.00): cacld. C 34.19, H 6.28, N 9.97; found C 34.01, H 6.59, N 9.52. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.51, 7.31 (s, NH, 2 H), 5.94, 5.96 (both s, NH_2, 4 H), 2.65, 2.06, 1.52, 1.48 (all m, C_6H_{10}, 10 H), 1.15 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30 MHz, [D$_6$]DMSO): δ = 189 ppm.

***trans,cis,cis*-[Pt(OH)(DACH)(DMSO)(NHCO*t*Bu)$_2$]Cl:** ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.82 (s, NH, 2 H), 6.00 (s, NH_2, 4 H), 2.51, 2.08, 1.52, 1.49 (m, C_6H_{10}, 10 H), 1.08 (s, $C(CH_3)_3$, 18 H) ppm. ^{195}Pt NMR (107.30, [D$_6$]DMSO): δ = –195 ppm.

X-ray Crystallographic Study: Single crystals of the complexes **4**–**7**, and **10** were grown by slow evaporation of solutions from the above-described preparations. In each case, suitable crystals were mounted on a glass fibre; the hemispheres of X-ray intensity data were collected with a Bruker Smart-*CCD* diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å). The first 50 frames were recollected at the end of the process to monitor crystal decay. The raw frame data were integrated into the SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[20] All structures were solved by direct methods and refined against F^2 by full-matrix least-squares techniques.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced into their calculated positions. Compounds **6**–**8** crystallize in noncentrosymmetric space groups. The absolute configurations were determined by refinement of the Flack x parameters. Details of the X-ray experiments and crystal data are summarized in Table 1.

CCDC-285359 (for **4**), -195437 (for **5**), -195438 (for **6**), -195439 (for **7**), and -195440 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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