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Organometallic Chemistry of an Amidate-Bridged Dinuclear Pt(III) Complex: Axial Pt(III)−Alkyl *σ*-Bond Formation in the Reaction with Acetone

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Amidate-bridged tetranuclear mixed-valent platinum complexes generally called “platinum-blues” and the related amidate-bridged dinuclear Pt(II) or Pt(III) complexes constitute an established class of compounds.[1−8] The complexes of general formula $[\mathrm{Pt^{III}_2(NH_3)_4L_2L'L''}]^{n+}$, where L is a deprotonated amidate bridging ligand, and L′ and L″ are axial ligands, exhibit reversible 2-electron redox behavior between Pt(III) and Pt(II), and have relatively loosely coordinated axial ligands trans to the Pt(III)−Pt(III) bond. These features make the compounds unique catalysts for selective oxidation of olefins by water oxygen to epoxides or ketones.[9] Oxidation of olefins to aldehydes and ketones by water oxygen is known as the Wacker reaction; however, oxidation to epoxides by water oxygen is unprecedented. These reactions suggest that olefins axially coordinate to the Pt(III)−Pt(III) axis at the initial stage of the reaction, and also suggest that other organometallic chemistry might be possible at the Pt(III)−Pt(III) axial position. In the present study, a Pt(III) dimer complex with an axial Pt(III)−carbon *σ*-bond has been isolated in the reaction with acetone in aqueous media. The structure, stability, and reactivity of the complex are reported.

Yellow plate crystals of pivalamidate-bridged Pt(III) dimer with an acetonate axial ligand, $[\mathrm{Pt_2(NH_3)_4(C_5H_{10}NO)_2(CH_2COCH_3)(NO_3)](NO_3)_2\cdot 2H_2O}$ (**1a**),[10] were prepared by adding $\mathrm{HNO_3}$ to an acetone solution of pivalamidate-bridged platinum-blue complex $[\mathrm{Pt_4(NH_3)_8(C_5H_{10}NO)_4](CF_3SO_3)_5}$ (**2a**),[10] which was prepared analogously to that in ref 5. The same compound with a different hydration number, $[\mathrm{Pt_2(NH_3)_4(C_5H_{10}NO)_2(CH_2COCH_3)(NO_3)](NO_3)_2\cdot H_2O}$ (**1b**),[10] was obtained by adding acetone to the condensed filtrate of $[\mathrm{Pt_4(NH_3)_8(C_5H_{10}NO)_4](NO_3)_5}$ (**2b**),[10] which was prepared analogously to that in ref 5. Pivalamidate-bridged Pt(III) complex without acetonate, head-to-head (HH) $[\mathrm{Pt_2(NH_3)_4(C_5H_{10}NO)_2(NO_2)(NO_3)](NO_3)_2\cdot H_2O}$ (**3**),[11] was prepared by dissolving either **2a** or **2b** in concentrated $\mathrm{HNO_3}$, followed by 2-fold dilution with $\mathrm{H_2O}$.

The ORTEP drawing of **1b** is shown in Figure 1.[12] Complex **1b** is a Pt(III) dimer with two pivalamidate ligands bridging the two Pt(III) atoms in a head-to-head (HH) manner. An axial Pt(III)−C(alkyl) bond trans to a Pt(III)−Pt(III) bond is very rare, only two precedents being known, $\mathrm{K_4[Pt_2(P_2O_5H_2)_4(CH_3)I]}$[13] and HH $[\mathrm{Pt_2(NH_3)_4(C_5H_5N_2O_2)_3](SiF_6)(NO_3)\cdot 7H_2O}$.[14] The latter compound has axial coordination by C5 of 1-methyluracilate. A Pt(III)−C *σ*-bond participating in bridging two Pt(III) atoms is known in $\mathrm{Cs_3[Pt_2(\mu\text{-}CH_2COO\text{-}C,O)_2(\mu\text{-}CH_3COO\text{-}O,O')_2Cl_2]Cl\cdot 3H_2O}$.[15]

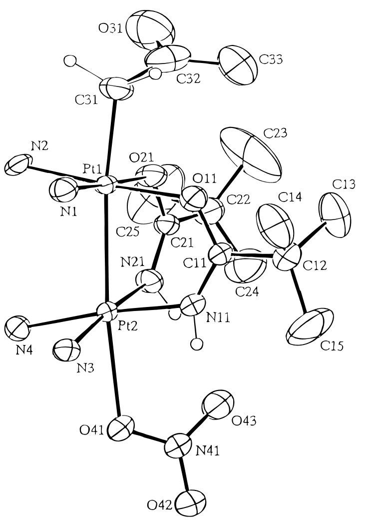

Figure 1. ORTEP drawing of $[\mathrm{Pt_2(NH_3)_4(C_5H_{10}NO)_2(CH_2COCH_3)(NO_3)](NO_3)_2\cdot H_2O}$ (**1b**).

The Pt−Pt distance of 2.6892(6) Å in **1b** is significantly longer than those of other amidate-bridged Pt(III) dimer complexes with axial ligands other than alkyls,[16,17] but is comparable to that in a 1-methylulacilate-bridged Pt(III) dimer complex with a Pt−C axial bond, HH $[\mathrm{Pt_2(NH_3)_4(C_5H_5N_2O_2)_3](SiF_6)(NO_3)\cdot 7H_2O}$ (2.685(1) Å).[14] The Pt−O(nitrate) distance is also affected by the strong trans influence through the Pt−Pt bond, the distance of Pt2−O41 (2.667(7) Å) in **1b** being remarkably longer than the Pt(III)−O(nitrate) distances in other amidate-bridged Pt(III) dimer complexes with axial ligands other than alkyls (2.165(10) to 2.36(3) Å).[16,17]

The ^{1}H, ^{13}C, and ^{195}Pt NMR spectra of **1** in aqueous solution show that **1** actually contains head-to-head (HH) and head-to-tail (HT) isomers,[18] both having an axial acetonate ligand.[19] Figure 2 shows the ^{1}H NMR signals of the $\mathrm{CH_2}^{-}$ region of the acetonate group, which clearly shows the existence of two sets of a five-line pattern. All other ^{1}H, ^{13}C, and ^{195}Pt NMR spectra consistently show the existence of the two isomers. The ^{195}Pt spectrum of **1** shows four peaks at −100, −623, −1368, and −1892 ppm relative to $\mathrm{Na_2PtCl_6}$ in $\mathrm{D_2O}$. The peaks at −100 and −1892 ppm show Pt satellites of $^{1}J(\mathrm{Pt-Pt}) = 3477$ Hz, whereas that of $\delta = -623$ and −1368 ppm was $^{1}J(\mathrm{Pt-Pt}) = 3625$ Hz. For reliable assignment of the Pt peaks, **1a** was prepared by using $^{15}\mathrm{NH_3}$ and [^{15}N]pivalamide, and the ^{195}Pt NMR spectrum (supporting information) was measured. Owing to the coupling with ^{15}N, the ^{195}Pt peaks could be assigned as follows: HH($\mathrm{N_2O_2C}$), −100 ppm; HT($\mathrm{N_3OC}$), −623 ppm; HT-

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(10) Anal. Calcd for **1a** ($\mathrm{C_{13}H_{41}N_9O_{14}Pt_2}$): C, 16.65; H, 4.41; N, 13.44. Found: C, 16.66; H, 4.17; N, 13.69. Anal Calcd for **1b** ($\mathrm{C_{13}H_{39}N_9O_{13}Pt_2}$): C,16.97; H, 4.27; N,13.70. Found: C, 16.91; H, 4.25; N, 13.66. Anal. Calcd for **2a** ($\mathrm{C_{25}H_{64}N_{12}O_{19}F_{15}S_5Pt_4}$): C, 14.56; H, 3.13; N, 8.15. Found: C, 14.67; H, 2.91; N, 7.92. Anal. Calcd for **2b** ($\mathrm{C_{20}H_{64}N_{17}O_{19}Pt_4}$): C, 14.76; H, 3.96; N, 14.63. Found: C, 14.76; H, 3.95; N, 14.29. The yields were 52%, and less than 10%, 16%, and 18% for **1a**, **1b**, **2a**, and **2b**, respectively.

(11) The structure of **3** has been confirmed by X-ray crystallography. The data are deposited as supporting information.

(12) Crystal data for **1b** at 23 °C. $M_r = 1627.19$, monoclinic, space group $P2_1/n$ (no. 14), $a = 19.299(5)$ Å, $b = 19.675(5)$ Å, $c = 13.168(3)$ Å, $\beta = 108.58(2)°$, $V = 4739(2)$ Å^3, $Z = 4$. For 5395 unique reflections with $F_o > 4\sigma(F_o)$, the final discrepancy indices were $R = 0.0612$ and $R_w = 0.0604$.

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(19) The isolated compound **1** seems to contain both isomers. In spite of our intensive effort, the crystal structure of what seems to be the HT isomer could not be solved with a reliable precision, because of the disorder of the amidate ligand.

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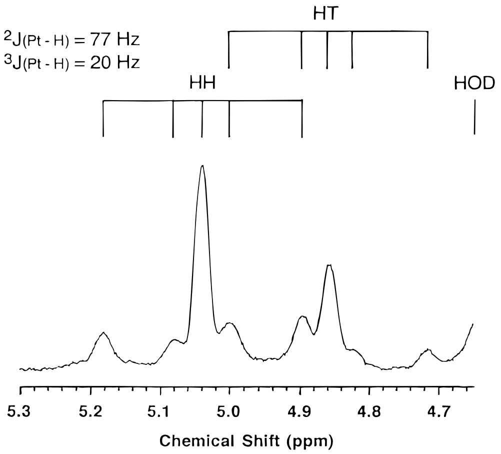
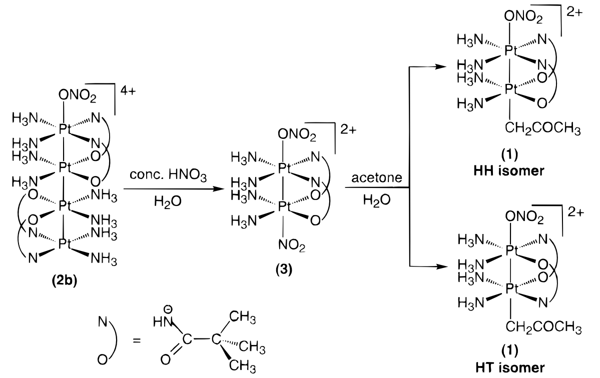


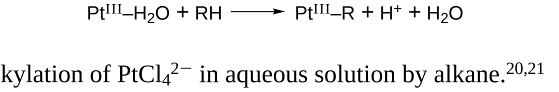
Figure 2. ^1H NMR spectrum of the CH_2^- region of **1** in D_2O at 44 °C. The temperature was raised to 44 °C in order to shift the HOD signal, which overlaps on the CH_2^- signal at room temperature. The measurement was carried out without sample spinning to avoid large side bands of HOD. No significant difference was observed in the HH to HT ratio between 44 °C and room temperature.

Scheme 1



(N_3O_2), −1368 ppm; and HH(N_4O), −1892 ppm. The atoms in parentheses indicate the coordinating atoms to the Pt atom. The Pt−N coupling constants are ^1J(Pt−N) = 304 Hz for $\delta = -100$ ppm, ^1J(Pt−N) = 254, 290, and 344 Hz for $\delta = -623$ ppm, ^1J(Pt−N) = 287, 329, and 370 Hz for $\delta = -1368$ ppm, and ^1J(Pt−N) = 276 and 367 Hz for $\delta = -1892$ ppm.

In the preparation procedure of **1**, **3** is first produced from **2a** or **2b** by nitric acid oxidation. Compound **1** is formed by the addition of acetone to **3**, as is shown in Scheme 1. Addition of excess acetone did not lead to coordination of the second acetone molecule at the other Pt atom. The coordination of acetone may proceed via initial coordination of the enol olefin of acetone to **3** (eq 1), or the coordination might occur via direct nucleophilic alkylation of the Pt(III) atom (eq 2), similar to the



$$Pt^{III}\text{–}H_2O \longrightarrow Pt^{III}\text{–}\overset{\|}{\underset{CH_3\ \ OH}{C}} \longrightarrow Pt^{III}\text{–}CH_2COCH_3 + H^+ \quad (1)$$

$$Pt^{III}\text{–}H_2O + RH \longrightarrow Pt^{III}\text{–}R + H^+ + H_2O \quad (2)$$

alkylation of $PtCl_4^{2-}$ in aqueous solution by alkane.[20,21] So far we have not noticed any alkane C−H activation in this aqueous system. An acidic condition is not always necessary for the preparation of **1**; however, it facilitates the formation since it avoids both reduction of the Pt(III) to Pt(II) by water[4] and deprotonation of the axially coordinated water in **3**. In our recent report on the oxidation of olefins by water oxygen catalyzed by amidate-bridged Pt(III) dimer complexes,[9] olefin coordination to a Pt(III)−Pt(III) axial position is postulated as the initial step of the reaction. If the formation of **1** proceeds similarly to the olefin oxidation, coordination of enol olefin seems plausible. However, direct alkylation (eq 2) also seems possible, considering the unexpectedly high stability of the Pt(III)−C bond in **1**. Although acidity-dependent conversion of σ-acetonyl complex $[Pt^{II}(CH_2COCH_3)(acetylacetonato)Cl]^-$ to the π-enol form has been reported,[24] no such conversion or equilibrium was observed in our system under the present experimental conditions.

Compound **1** produces hydroxyacetone, when dissolved in 10 mM NaOD,[22] whereas it gives bromoacetone on addition of a 50-fold concentration of NaBr.[23] These reactions proceed almost quantitatively, with concomitant reduction of the Pt(III) dimer to a Pt(II) dimer, $[Pt^{II}_2(NH_3)_4(C_5H_{10}NO)_2]^{2+}$. Compound **1** releases acetonylacetone with a yield of 40% under irradiation of a Hg lamp. These facts suggest that **1** undergoes nucleophilic attack without light irradiation, whereas the alkyl ligand behaves as a radical under UV irradiation. Interestingly, the coordinated acetonate ligand can be transferred to another amidate-bridged Pt(III) dimer; on addition of α-pyrrolidonate-bridged Pt(III) dimer complex $[Pt_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2{\cdot}H_2O$ (**4**)[16] to a solution of **1,** a new Pt(III) dimer complex, $[Pt_2(NH_3)_4(C_4H_6NO)_2(CH_2COCH_3)L]^{n+}$ (**5**) (L is probably H_2O), was observed in the ^1H NMR spectrum after several hours of reaction.[25] The new signals were also observed in an independent reaction of **4** with a large excess of acetone at room temperature for 4 days. Since, in the absence of **3**, a large excess of acetone is necessary to form **5** from **4**, it is concluded that the acetonate of **1** is more easily transferable than free acetone to **4**. This fact shows that the acetonate of **1** is still capable of alkylating Pt(III) dimer complexes by using its terminal acyl group. Although alkene insertion to Pt(II)−H bonds is widely known,[26] it is surprising that a ketone reacts so easily with a Pt(III) dimer to form a stable alkyl compound in H_2O. The novel electrophilic reactivity of the alkyl group in **1** must be a result of the strong electron-withdrawing effect of the unusually high oxidation state of Pt(III). The reaction of the coordinated acetonate with OH^- to release hydroxyacetone corresponds to net oxidation of a C−H bond, and is reminiscent of C−H activation of alkane by $PtCl_4^{2-}$ and $PtCl_6^{2-}$,[20,21] where Pt(IV)−R acts as an electrophile, whereas Pt(II)−R is a nucleophile. Presumably Pt(III) acts similarly to Pt(II) at the stage of the alkyl coordination, whereas it acts similarly to Pt(IV) when the coordinated alkyl ligand reacts with OH^-. Such flexibility of the Pt oxidation state is made possible by the delocalized electronic state through the Pt(III)−Pt(III) bond. A wider variety of reactions is expected to this distinct Pt(III) compound.

Supporting Information Available: Details of the preparation procedures for **1**, **2**, and **3**, tables of position and thermal parameters, bond lengths and angles, and crystallographic data for **1b** and **3**, ORTEP drawing for **3**, ^1H, ^{13}C, and ^{195}Pt NMR spectra of **1**, and ^1H and ^{195}Pt NMR spectra of **3** (30 pages). See any current masthead page for ordering and Internet access instructions.

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(22) ^1H NMR chemical shifts (ppm) of the products: 1.067 (Me of pivalamidate in the Pt(II) dimer), 2.16 (Me of hydroxyacetone), 4.37 (methylene of hydroxyacetone).

(23) ^1H NMR chemical shifts (ppm) of the products: 1.067 (Me of pivalamidate in the Pt(II) dimer), 2.32 (Me of bromoacetone), 4.31 (methylene of bromoacetone).

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(25) The three methylene signals in the ^1H NMR spectrum of **4** (2.2−2.4 (m, H4), 2.8−3.0.(m, H3), 3.7−3.8 (m, H5) ppm) decreased, and new signals of **5** appeared at 2.19 (quintet, H4), 2.77 (t, H3), 3.73 (t, H5), 2.25 (s, Me of acetonate), and 5.02 (s, methylene of acetonate) ppm.

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