

Synthesis and Characterization of Stable Bis(methoxo)platinum(IV) Complexes. A Facile Synthesis via Fluorenylidene-philic Interactions

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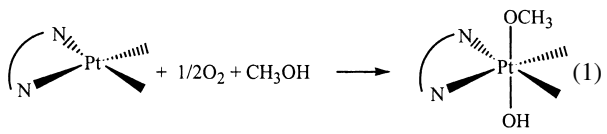
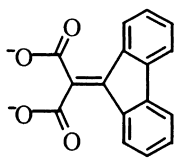
Stable mono- and bis(methoxo)platinum(IV) species via the oxidation of Pt^{II} to Pt^{IV} have been prepared and characterized. The reaction of [Pt^{II}(fpd)(dpda)] (fpd = 9-fluorenylidenepropanedioate; dpda = 2,2-dimethyl-1,3-propanediamine) with hydrogen peroxide in methanol at room temperature affords [$Pt^{IV}(OH)(OCH_3)$(fpd)(dpda)], and further reaction at boiling methanol produces a bis(methoxo)platinum(IV) compound, [$Pt^{IV}(OCH_3)_2$(fpd)(dpda)]. The bis(methoxo)platinum(IV) compound can be prepared by the direct reaction of [Pt^{II}(fpd)(dpda)] with hydrogen peroxide in boiling methanol or by the simple stirring of [$Pt^{IV}(OH)_2$(fpd)(dpda)] in boiling methanol. The crystal structures of [Pt^{II}(fpd)(dpda)]·$2(CH_3)_2NCHO$ (*Pna*2_1, a = 10.125(2) Å, b = 26.141(4) Å, c = 10.845(6) Å, V = 2870(2) Å^3, Z = 4, R = 0.0370), [$Pt^{IV}(OH)_2$(fpd)(dpda)]·$3C_2H_5OH$ ($P2_1/a$, a = 10.312(2) Å, b = 22.044(5) Å, c = 14.225(3) Å, β = 110.25(2)°, V = 3034(1) Å^3, Z = 4, R = 0.0572), and [$Pt^{IV}(OCH_3)_2$(fpd)(dpda)]·$1.5CH_3OH$·$0.5C_2H_5OH$·$0.5H_2O$ ($P\bar{1}$, a = 13.333(2) Å, b = 15.386(3) Å, c = 18.446(5) Å, α = 66.80(2), β = 69.06(2)°, γ = 68.84(1), V = 3140(1) Å^3, Z = 2, R = 0.0437) have been solved and refined. For [$Pt^{IV}(OCH_3)_2$(fpd)(dpda)], the 9-fluorenylidene moiety of fpd ligand snugly interacts with the methoxo group (C(22)···C(9), 3.34 Å; C(22)-H···C(9), 2.65 Å). The mono- and bis(methoxo)platinum(IV) compounds are stable even in solution.

Oxidations of Pt^{II} to Pt^{IV} compounds have been utilized in various aspects of platinum chemistry such as the formation of mixed valence compounds, the synthesis of oral antitumor (pro)drugs, and the elucidation of reaction mechanisms.[1–5] The platinum(IV) chemistry has been largely based on hydroxo complexes obtained by the oxidation of the corresponding Pt^{II} with hydrogen peroxide, and the study has recently been extended to chloro and carboxylato analogs. Alkoxoplatinum(IV) have been relatively less explored, even though alkoxoplatinum compounds have recently attracted attention.[6–8] Thus, alkoxoplatinum(IV) chemistry have been limited to mono(alkoxo)platinum(IV) owing to labile and reducible Pt-oxo linkages. For instance, admission of O_2 to a methanolic solution of Pt^{II} gave mono(methoxo)platinum(IV) complexes (Eq. 1).[9] Hydrogen peroxide oxidation in alcohol resulted in the formation of mono(alkoxo)platinum(IV) complexes.[2] To date, bis(alkoxo)platinum(IV) complexes have remained unexplored.



(1)

This article reports the synthesis and related properties of stable [$Pt^{IV}(OCH_3)_2$(fpd)(dpda)] (fpd = 9-fluorenylidenepropanedioate (Chart 1); dpda = 2,2-dimethyl-1,3-propanediamine) and related compounds via a unique intramolecular fluorenylidene-philic interaction. Specific noncovalent interactions play critical roles in the preparation and stability of unique structures.[10–12] Previously, we reported the conformational induction by unusual interaction assistance as a communication.[13] The present results are of particular interest because the compound represents the first example of a stable bis(alkoxo)platinum(IV) complex.



fpd

Chart 1.

Experimental

Materials and Measurements. Reagent grade potassium tetrachloroplatinate(II) (Kojima) was used as received. [Pt^{II}(fpd)(dpda)] (**1**) and [$Pt^{IV}(OH)(OCH_3)$(fpd)(dpda)] (**3**) were prepared by the respective literature methods.[13] ^{1}H NMR spectra were recorded on a Varian Gemini 300 or a Bruker 600 instrument operating at 300.00 or 600.00 MHz, respectively. The chemical shifts were relative to internal Me_4Si. The infrared spectra in the 4000–400 cm^{-1} region were measured on a Perkin Elmer 16F PC model FT-IR spectrophotometer. Elemental analyses were performed at the Advanced Analysis Center at KIST.

[$Pt^{IV}(OH)_2$(fpd)(dpda)] (2). A 30% aqueous solution of H_2O_2 (1 mL) was added to a solution of **1**·$2(CH_3)_2NCHO$ (0.71 g, 1.0 mmol) in acetone (20 mL). The mixture solution was then stirred for 4 h at room temperature. After the solid material had

Table 1. Crystallographic Data for **1**·2$(CH_3)_2$NCHO, **2**·3C_2H_5OH, and **4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O

	1·2$(CH_3)_2$NCHO	**2**·3C_2H_5OH	**4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O
Formula	$C_{21}H_{22}N_2O_4Pt$·2C_3H_7NO	$C_{21}H_{24}N_2O_6Pt$·3C_2H_5OH	$C_{51}H_{76}N_4O_{17}Pt_2$
F.w.	707.69	733.72	1407.34
Space group	$Pna2_1$(33)	$P2_1/a$(14)	$P\bar{1}$(2)
a/Å	10.125(2)	10.312(2)	13.333(2)
b/Å	26.141(4)	22.044(5)	15.386(3)
c/Å	10.845(6)	14.225(3)	18.446(5)
α/deg			66.80(2)
β/deg		110.25(2)	69.06(2)
γ/deg			68.84(1)
V/Å^3	2870(2)	3034(1)	3140(1)
Z	4	4	2
d_{cal}/g cm^{-3}	1.638	1.606	1.489
μ, mm^{-1}	4.934	4.677	4.514
R $\{I > 2\sigma(I)\}$	$R1$ = 0.0370	0.0572	0.0437
	w$R2$ = 0.0858	0.1063	0.1145

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = \Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^2)^{1/2}$

been filtered off, the filtrate was evaporated to dryness. The crude product was recrystallized in a mixture of water/ethanol (1:1) to give colorless crystals suitable for X-ray crystallography in 81% yield. mp 138 °C (dec). Anal. Calcd for $C_{21}H_{24}N_2O_6Pt$·3C_2H_5OH: C, 44.20; H, 5.77; N, 3.82%. Found: C, 44.60; H, 5.58; N, 3.90%. IR (KBr, cm^{-1}) ν(OH), 3448; $\nu(COO)_{asym}$, 1666, 1611; $\nu(COO)_{sym}$, 1368, 1322. ^{1}H NMR ($(CH_3)_2SO$-d_6) δ 0.80 (s, 3H, CH_3), 1.94 (br, 2H, CH_2), 6.78 (br, 2H, NH_2), 7.23 (t, J = 7.3 Hz, 1H, PhH), 7.37 (t, J = 7.3 Hz, 1H, PhH), 7.81 (d, J = 7.6 Hz, 1H, PhH), 8.06 (t, J = 7.6 Hz, 1H, PhH), 10.19 (s, 1H, OH).

[Pt^{IV}(OCH$_3$)$_2$(fpd)(dpda)] (4). **3**·2CH_3OH (0.67 g, 1.0 mmol) was refluxed in methanol for 2 h. After the solid material was filtered off, the filtrate was condensed to 5 mL, to this excess diethyl ether was added to obtain solid product. The crude product was recrystallized in a mixture solvent of water/methanol/ethanol (1:1:1) to obtain colorless crystals suitable for X-ray crystallography (83% yield). mp 153 °C (dec). Elemental analysis (C, H, N) gave erratic results presumably due to the partial evaporation of solvate methanol and ethanol molecules. ^{1}H NMR ($(CH_3)_2$NCHO-d_7) δ0.80 (s, 3H, CH_3), 1.81 (br, 2H, CH_2), 2.65 (s, 3H, OCH_3), 6.51 (br, 2H, NH_2), 7.30 (t, J = 7.3 Hz, 1H, PhH), 7.45 (t, J = 7.4 Hz, 1H, PhH), 7.61 (d, J = 7.5 Hz, 1H, PhH), 8.17 (d, J = 7.8 Hz, 1H, PhH). IR (KBr, cm^{-1}) $\nu(COO)_{asym}$, 1662, 1621; $\nu(COO)_{sym}$, 1320.

The reaction of **1** with H_2O_2 in boiling methanol gave **4**. **2** in boiling methanol converted to the product, **4**.

Crystal Structure Determination. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) at ambient temperature (20(1) °C). The unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects, and empirically for absorption (azimuthal ψ-scans of six reflections). The structures were solved by the Patterson method (SHELXS-97), and were refined by full-matrix least squares techniques (SHELXL-97).[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Further details concerning the crystal structure investigation of **1**·2$(CH_3)_2$NCHO, **2**·3C_2H_5OH, and **4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, (U.K.). The complete F_o–F_c data have been deposited as Document No. 75033 at the Office of the Editor of Bull. Chem. Soc. Jpn.

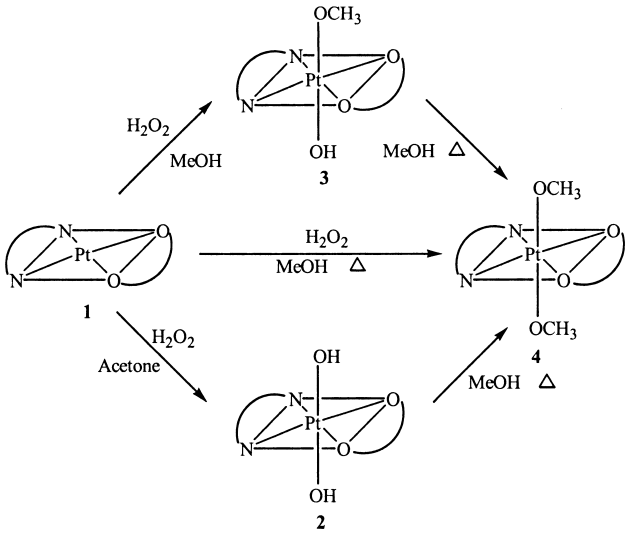
Results and Discussion

Synthesis. The oxidation of **1** with a 30% aqueous solution of H_2O_2 in methanol produced a mono(methoxo)platinum(IV) species, **3**, at room temperature and a bis(methoxo)platinum(IV), **4**, in boiling methanol. The hydrogen peroxide oxidation of **2** in acetone afforded only bis(hydroxo)platinum(IV), **3** further reaction in boiling methanol gave **4**. Of course, the bis(methoxo)platinum(IV) species could be prepared by the direct oxidation of **1** with H_2O_2 in boiling methanol. The overall reactions are depicted in Scheme 1. The most interesting feature is that all the species can be smoothly isolated by the reaction conditions. The products were not affected by the change of mole ratio of reactants, but could be affected by the reaction time. All the platinum(IV) compounds are stable pale yellow crystalline solids. The compounds including the bis(methoxo)platinum(IV) compound are soluble in common organic solvents and are stable in solution.

[Pt^{II}(fpd)(dpda)]·2(CH$_3$)$_2$NCHO. The crystal structure of **1** is depicted in Fig. 1, and selected bond distances and angles are listed in Table 2. The local geometry around the platinum atom approximates a typical square planar arrangement. The bond lengths and angles (Pt–N(1) = 1.96(2); Pt–N(2) = 2.07(2); Pt–O(1) = 2.09(1); Pt–O(3) = 1.98(2) Å; N(1)–Pt–N(2) = 95.5(4); N(1)–Pt–O(1) = 176.1(7); O(2)–Pt–N(2) = 172.8(7); O(1)–Pt–O(2) = 90.9(4)°) are not exceptional.[15,16] Both fpd and dpda ligands are chelated to the platinum(II). The 9-fluorenylidene (flu) group of the fpd is bent from the platinum square plane (dihedral angle between the two planes = 94.9(2)°).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**·2$(CH_3)_2$NCHO, **2**·3C_2H_5OH, and **4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O

	1·2$(CH_3)_2$NCHO	**2**·3C_2H_5OH	**4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O
Pt–O(1)	2.09(1)	2.02(1)	2.026(7)
Pt–O(2)	1.98(2)	2.00(1)	2.023(7)
Pt–O(5)		2.01(1)	1.995(7)
Pt–O(6)		1.99(1)	1.996(7)
Pt–N(1)	1.96(2)	2.00(1)	2.031(9)
Pt-N(2)	2.07(2)	1.98(1)	2.019(8)
O(1)–Pt–O(2)	90.9(4)	93.0(5)	93.4(3)
O(1)–Pt–N(2)	82.0(7)	85.5(5)	86.8(3)
O(1)–Pt–N(1)	176.1(7)	176.7(6)	176.6(3)
O(2)–Pt–N(2)	172.8(7)	174.4(5)	178.7(3)
N(1)–Pt–N(2)	95.5(4)	94.0(6)	94.3(4)
N(1)–Pt–O(2)	91.6(7)	87.2(5)	85.4(3)



Scheme 1.

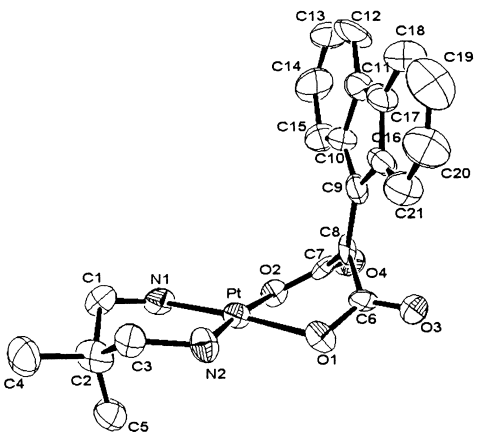


Fig. 1. ORTEP drawings of **1**·2$(CH_3)_2$NCHO showing the atomic labeling scheme and thermal ellipsoids at the 50% level. Solvate *N*,*N*-dimethylformamide molecule and hydrogen atoms are omitted for clarity.

$[Pt^{IV}(OH)_2(fpd)(dpda)]$·3$C_2H_5OH$. The crystal structure

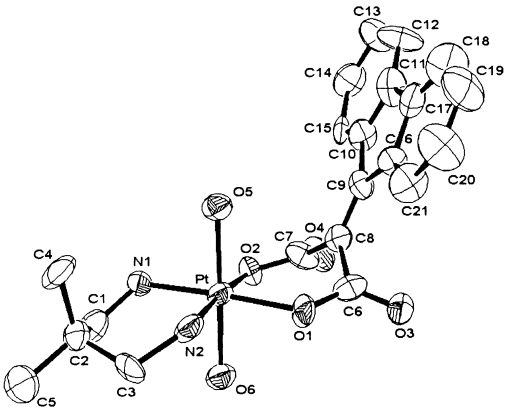


Fig. 2. ORTEP drawings of **2**·3C_2H_5OH showing the atomic labeling scheme and thermal ellipsoids at the 50% level. Solvate ethanol molecule and hydrogen atoms are omitted for clarity.

of **2** is shown in Fig. 2, and relevant bond lengths and angles are not exceptional (Table 2). The local geometry around the platinum atom is an octahedral arrangement with the two added hydroxo ligands in *trans* coordination sites (O(5)–Pt–O(6) = 176.8(5)°). The flu moiety is still bent (113.0(4)°), and thus the interacting distance of C(9)···O(5) is 3.56 Å. The flu moiety of each molecule π-interacts with its neighboring molecule in the solid state (3.5–4.0 Å). ^{1}H NMR spectra are consistent with the X-ray crystal structure data, indicating that the structure is retained and stable in solution.

$[Pt^{IV}(OCH_3)_2(fpm)(dpda)]$·1.5$CH_3OH$·0.5$C_2H_5OH$·0.5$H_2O$. There are two independent molecules in an asymmetric region of the monoclinic unit cell, the features of the two molecules are within error of being identical. One of the molecules and its labeling scheme is depicted in Fig. 3, and bond lengths and angles are listed in Table 2. The local geometry around the platinum(IV) approximates to a typical octahedral arrangement with the two methoxo groups in *trans* positions. The fpd ligand is chelated to the Pt^{IV} in two equatorial sites. The neutral amine is inevitably chelated to the platinum(IV) in *cis* positions to provide a suitable bite angle. One axial methoxo group parallels with the flu at the distances of usual

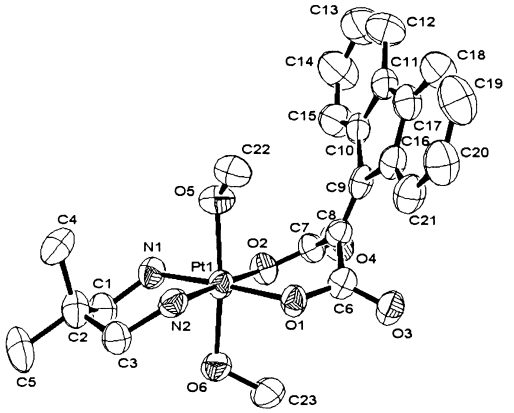


Fig. 3. ORTEP drawings of **4**·1.5CH_3OH·0.5C_2H_5OH·0.5H_2O showing the atomic labeling scheme and thermal ellipsoids at the 50% level. Solvate molecules and hydrogen atoms are omitted for clarity.

C(H)···π interaction (C(22)···C(9), 3.33 Å), indicating that the flu interacts with the methoxo group.[13] The bent angle between the fpd and the platinum square plane is 106.4(2)°, which is slightly smaller than that (113.0(4)°) of **2**. The difference between the two bent angles shows that the flu moiety more strongly interacts with CH_3O than with OH. Thus, the O(5)–Pt(1)–O(6) angle (173.4(3)°) is slightly smaller than that of **2** (176.8(5)°).

To investigate the behavior in solution, the ^{1}H NMR of **4** was measured in DMF-d_7. Broadened peaks at 6.51 (NH_2), 2.81 (NCH_2), and 2.65 ppm (OCH_3) suggest that a constraint via the flu···OCH_3 interaction exists in solution. Furthermore, the proton resonances exhibit a marked temperature-dependence in a mixture of $(CH_3)_2NCHO$-d_7 and $(CH_3)_2SO$-d_6 in the temperature range 15–45 °C (Fig. 4). The two CH_3O groups display a pair of resonances (2.84 and 2.40 ppm) at 15 °C. Warming the sample results in coalescing to a singlet at 30 °C, and sharpening at 45 °C. The fluxional process indicates an interconversion between "bent-up" and "bent-down" of the flu at elevated temperature. The high field shift at 2.84 ppm is explained in terms of a π-shielding effect via the flu···OCH_3.

Stability and Related Properties of Bis(methoxo)platinum(IV). To date, bis(methoxo)platinum(IV) species were not synthesized presumably owing to the labile properties of Pt-oxo bonds. In contrast, Scheme 1 shows that **4** can be prepared via various procedures, indicating that the compound is a stable species. Actually the bis(methoxo)platinum(IV) compound is stable both in the solid state and in solution. The preparation and stability of the compound seems to be induced from the extra flu···OCH_3 interaction (Scheme 2). One methoxo moiety behaves like a stable (pseudo)bridging group. This case presents a good example of how unique noncovalent interactions play critical roles in the preparation and stability of products. Easy isolations of both mono(methoxo)platinum(IV) and bis(methoxo)platinum(IV) are very rare. Such a consecutive alkoxylation may result from the order of flu-philicity of $OCH_3 > OH$.[13] In particular, the mono(methoxo)platinum(IV) complex may afford various mixed-ligand platinum(IV) complexes. Thus, for the present reaction, the flu interaction is not a simple weak interaction, but is probably an important factor

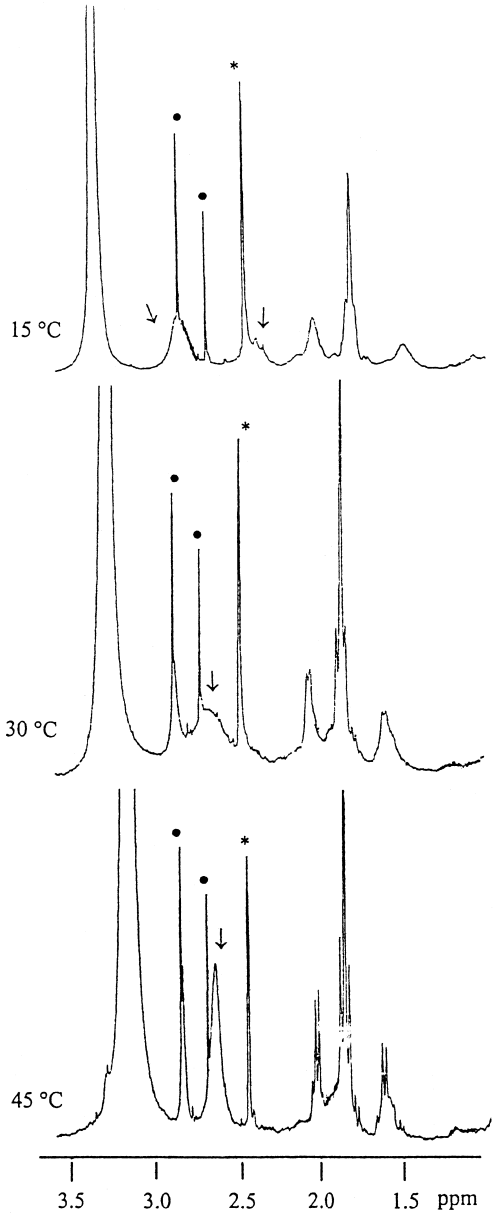
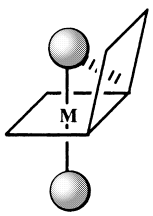


Fig. 4. Variable temperature ^{1}H NMR spectra (1.5–4.5 ppm) of **4** in a mixture of $(CH_3)_2NCHO$-d_7 and $(CH_3)_2SO$-d_6 (600 MHz). ∗ indicates Me_2SO, and • designates Me_2-NCHO. The strong peak at 3.2 ppm was induced by water. The satellites around 1.9 ppm were induced by the isotope of Pt^{IV}.



Scheme 2.

for the preparation and stability of the product. What is the driving force of the flu interaction? The electron donor ability

of the flu moiety may contribute as a critical factor of the flu interaction. Even though the fpd ligand is an α, β-unsaturated carboxylic acid, the bending prevents delocalization of its π electrons. As a proof of the localization, the bond length (1.33(2) Å for **2**; 1.34(1) Å for **4**) of the double bond C(3)–C(4) corresponds to that (1.34 Å) of a normal ethylene group,[17] indicating that the flu moiety is electron-rich.

In conclusion, our works have shown that the H_2O_2 oxidation of [Pt^{II}(fpd)] in alcohols is an useful route to complexes of the general formula [$Pt^{IV}(OR)_n$(fpd)] (n = 1, 2). The route to bis(alkoxo) complexes is valuable since such platinum(IV) complexes were not previously known. The noncovalent interaction-assistance concept as an effective strategy may apply to the design and synthesis of structural components, including desirable mixed ligand complexes.

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