Communication

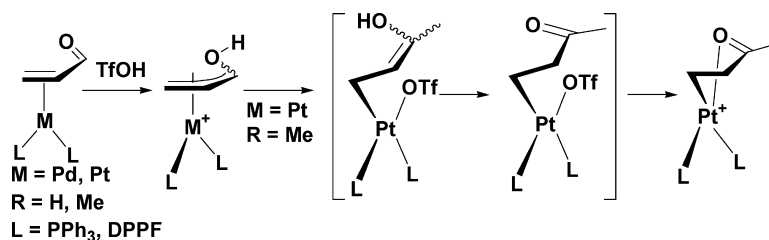# Synthesis, Structure, and Reactivity of a □-1-Hydroxyallyl Complex: Protonation of an □,β-Unsaturated Carbonyl Compound Bound to Palladium(0) and Platinum(0)

Sensuke Ogoshi, Masaki Morita, and Hideo Kurosawa

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Synthesis, Structure, and Reactivity of a η³-1-Hydroxyallyl Complex: Protonation of an α,β-Unsaturated Carbonyl Compound Bound to Palladium(0) and Platinum(0)

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Although η^3-allyl transition metal complexes have been well studied, only a limited number of η^3-hydroxyallyl complexes have been reported.[1] The potential of η^3-hydroxyallyl complexes for organic synthesis appears very high, because an appropriate transformation of η^3-hydroxyallyl complex would allow us to introduce a C3 unit bearing oxygen into organic products. So far, only η^3-2-hydroxyallyl complexes have been investigated as a derivative of oxatrimethylenemethane (OTMM) complexes, in which the reversible interconversion between η^2-OTMM and η^3-2-hydroxyallyl complexes by addition or abstraction of a proton has been reported (Scheme 1).[1c] On the other hand, the regioisomer, η^3-1-hydroxyallyl complex, has not been reported yet.[2] In view of the reaction of η^2-enonepalladium complexes with Lewis acid to give zwitterionic η^3-1-metalloxyallylpalladium complexes,[3] an attractive route to η^3-1-hydroxyallyl complexes is the addition of a proton to η^2-enone complexes (Scheme 2). However, a proton could also undergo electrophilic addition at the metal center to generate a metal hydride complex, as in the reaction of Pd-(PMePh$_2$)$_2$(CH$_2$=CHPh) with HCl to give Pd(H)(Cl)(PMePh$_2$)$_2$.[4] If hydride is formed, there would be little chance for the formation of η^3-1-hydroxyallyl complex, because the hydride and enone would give β-ketoalkyl and η^3-oxaallyl complexes, as suggested by van Leeuwen and co-workers (Scheme 3).[5] For the development of new η^3-allylmetal chemistry, it seems of fundamental value to examine how efficiently the method of Scheme 2 works. We describe the synthesis, structure, and reactivity of η^3-1-hydroxyallyl complexes of palladium and platinum. Moreover, we propose the isomerization path from η^3-1-hydroxyallyl to β-ketoalkyl via tautomerization in an η^1-allyl coordination mode.
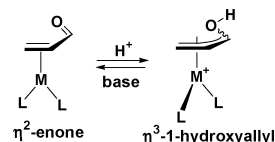
The reaction of η^2-enonepalladium complex with TfOH gave a palladium complex (**1a**−**c**) having expected composition in elemental analysis (eq 1).[6] The ¹H, ³¹P, and ¹³C NMR spectra indicate that these complexes have an η^3-hydroxyallyl structure or an intermediate structure between an η^3-hydroxyallyl and a proton coordinated η^2-enone structure.[3] **1a** does not transform into its isomers, β-ketoalkylpalladium **3a** or η^3-oxaallylpalladium **4a** (M = Pd, L$_2$ = DPPF in Scheme 3). These complexes **3a** and **4a** were reported to undergo mutual isomerization at room temperature via the insertion of methylvinyl ketone (MVK) into hydridopalladium species formed by the β-H elimination (Scheme 3).[5] During such interconversion, there was no indication of the formation of η^3-1-hydroxyallyl complex. Moreover, neither **3a** nor **4a** was observed in the reaction of Pd(dppf)(mvk) with TfOH. Thus, η^3-1-hydroxyallyl complexes would not have been formed via hydride palladium species but via the direct addition of a proton to the carbonyl oxygen of the coordinated enone.

The structure of **1b** and **1c**, determined by X-ray diffraction analysis, is consistent with the anticipated structure (Figures 1 and 2).[7] The complex **1b** is the first example of the η^3-1-hydroxyallyl transition metal complex. The Pd−C3 bond distance (2.29 Å) in
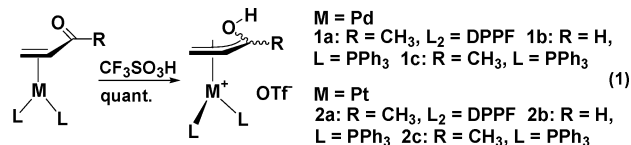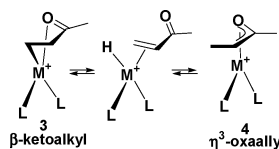
Scheme 1

Scheme 2

Scheme 3

(1)

M = Pd
1a: R = CH₃, L₂ = DPPF **1b**: R = H, L = PPh₃ **1c**: R = CH₃, L = PPh₃
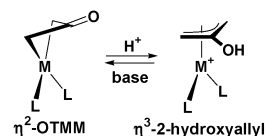
M = Pt
2a: R = CH₃, L₂ = DPPF **2b**: R = H, L = PPh₃ **2c**: R = CH₃, L = PPh₃

1b is normal as in the η^3-allylpalladium complex, while it is somewhat longer in **1c** (2.73 Å).[8] However, the latter is much shorter than that in the η^2-enonepalladium complex,[3] which indicates significant contribution of the η^3-1-hydroxyallyl structure to **1c**. The relatively short distance between the two oxygen atoms in the carbonyl group and TfO⁻ (2.91 Å for **1b**, 2.70 Å for **1c**) suggests the existence of a hydrogen bond. This hydrogen bond would lengthen the bond between palladium and carbonyl carbon. The corresponding complex having B(C₆F₅)₄⁻ as a counteranion (**1c′**: major/minor = 65/35) prepared by the treatment of **1b** with LiB-(C₆F₅)₄ shows the larger P−P coupling constant, probably due to the stronger Pd−C3 bond[9] caused by a weaker hydrogen bond involving B(C₆F₅)₄⁻. Addition of pyridine (1 equiv) to the solution of **1b** in CD₂Cl₂ led to the formation of a mixture of (η^2-acrolein)-Pd(PPh₃)₂ and **1b** (56/44), which indicates that the pK_a value for **1b** is very close to that of pyridine·H⁺ (pK_a = 5.22). For comparison, the pK_a of (η^3-2-hydroxyallyl)Pd(PPh₃)₂ in aqueous MeOH is ca. 7.[1c]

The analogous η^3-1-hydroxyallylplatinum complexes **2a**, **2b**, and **2c** were also prepared by the same method. Complexes **2a** and **2c** isomerized slowly to the corresponding β-ketoalkylplatinum complexes (**5a**, **5c**) at room temperature (Scheme 4),[10] although complex **2b** did not undergo isomerization under the same condition. The spontaneous isomerization may proceed via an η^1-1-hydroxyallyl
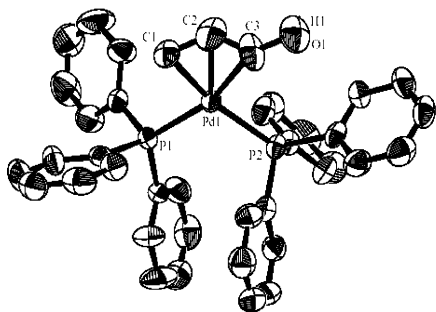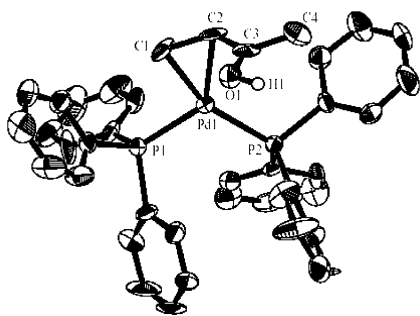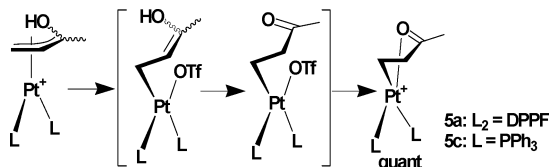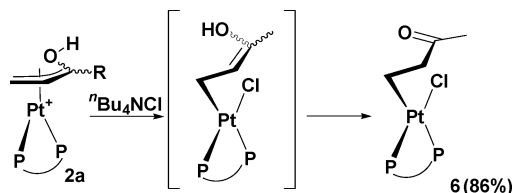
Figure 1. Molecular structure of **1b**.

Figure 2. Molecular structure of **1c**.

Scheme 4. Spontaneous Isomerization

Scheme 5. Transformation into the η^1-β-Ketoalkyl Complex

allylpalladium complex did not undergo isomerization to the corresponding β-ketoalkyl palladium complex. On the other hand, the η^3-1-hydroxyallylplatinum complex isomerized to the corresponding β-ketoalkyl complex, in which tautomerization would occur in the η^1-allyl coordination mode.

Supporting Information Available: Experimental procedures (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

intermediate. The occurrence of the η^1-allyl coordination mode would promote tautomerization from enol to keto, which could not occur in the η^3-allyl coordination mode. In fact, addition of Bu$_4$-NCl to **2a** led to the formation of the η^1-β-ketoalkylplatinum complex (**6**) via the η^1-1-hydroxyallyl complex (Scheme 5).[11] Because Pt(H)(Cl)(dppf)[12] did not react with MVK, an alternative route from **2a** to **6** via formation of Pt(H)(Cl)(dppf) and its reaction with MVK would be ruled out. The greater ease of the isomerization for **2c** than **2b** would be attributed to the larger contribution of η^3-allyl structure in **2b** than in **2c**, which can be deduced from the comparison of the X-ray structures of **1b** and **1c**. Similarly, the failure of the corresponding palladium complexes, **1a** and **1c**, to isomerize to **3** (and **4**) could be rationalized by the highly stable η^3-allyl coordination mode of these complexes, because palladium prefers η^3-coordination to η^1-coordination of the allyl ligand to a greater extent than platinum.[13]

In summary, we demonstrated that the direct addition of a proton to a carbonyl oxygen in the η^2-enone complex of palladium and platinum led to the quantitative formation of η^3-1-hydroxyallyl complexes of palladium and platinum, of which X-ray diffraction analysis showed typical η^3-allyl structure. Moreover, η^3-1-hydroxy-

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(6) General procedure for **1b**: To a solution of Pd(CH$_2$=CHCHO)(PPh$_3$)$_2$ (119.3 mg, 0.1736 mmol) in 5 mL of THF was added 15.3 μL of TfOH (26.1 mg, 0.1741 mmol) at room temperature, and the solution color changed from pale yellow to orange. The reaction mixture was concentrated in vacuo to give brown solids quantitatively. The solids were washed with hexane to give 128.1 mg of the complex **1b** in 88% (syn/anti = 18/82) isolated yield. Selected spectral data for syn isomer, ^{1}H NMR (CD$_2$-Cl$_2$): δ 3.28 (t, J = 8.6 Hz, 1H), 4.56 (m, 1H), 7.06 (t, J = 5.2 Hz, 1H). ^{31}P NMR (CD$_2$Cl$_2$): δ 20.36 (d, J_{PP} = 38.4 Hz), 30.61 (d, J_{PP} = 38.4 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 57.4 (d, J_{CP} = 29.8 Hz), 88.6 (dd, J_{CP} = 3.4, 6.1 Hz), 141.1 (dd, J_{CP} = 3.7, 10.1 Hz, *C*OH). Anti isomer, ^{1}H NMR (CD$_2$Cl$_2$): δ 2.43 (dt, J = 2.4, 11.0 Hz, 1H), 3.22 (dt, J = 3.2, 7.9 Hz, 1H), δ 5.45 (dd, J = 11.2, 19.6 Hz, 1H), 6.78 (dd, J = 8.8, 10.8 Hz, 1H), 7.16−7.85 (m, 30H). ^{31}P NMR (CD$_2$Cl$_2$): δ 24.66 (d, J_{PP} = 34.1 Hz), 27.90 (d, J_{PP} = 34.1 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 59.4 (dd, J_{CP} = 2.3, 27.9 Hz), 95.9 (dd, J_{CP} = 3.1, 5.9 Hz), 128.9 (dd, J_{CP} = 4.4, 10.3 Hz), 130.8 (dd, J_{CP} = 2.3, 14.6 Hz), 132.1 (dd, J_{CP} = 1.4, 40.7 Hz), 133.8 (dd, J_{CP} = 3.0, 13.3 Hz), 141.4 (dd, J_{CP} = 2.8, 26.5 Hz, *C*OH). Anal. Calcd for C$_{40}$H$_{35}$F$_3$O$_4$P$_2$Pd$_1$S$_1$ (a mixture of syn and anti isomers): C, 57.39; H, 4.21. Found: C, 56.95; H, 4.37.

(7) X-ray data for **1b**. M = 837.12, yellow, monoclinic, $P2_1/c$ (No. 14), a = 11.8091(5) Å, b = 18.3006(7) Å, c = 17.807(1) Å, β = 103.656(1)°, V = 3739.6(3) Å^3, Z = 4, D_{calcd} = 1.487 g/cm^3, T = 0.0 °C, R (R_W) = 0.070 (0.093). X-ray data for **1c**. M = 851.14, yellow, orthorhombic, $Pna2_1$ (No. 33), a = 21.429(1) Å, b = 12.8667(8) Å, c = 14.2909(6) Å, V = 3940.3(3) Å^3, Z = 4, D_{calcd} = 1.435 g/cm^3, T = 0.0 °C, R (R_W) = 0.078 (0.126).

(8) A similar influence of the substituent group at C3 on the Pd−C3 bond distance has been reported.[3]

(9) A larger coupling constant indicates a shorter Pd−C3 bond length[3] (**1c**, 35.3 and 29.3 Hz; **1c′**, 36.9 and 34.1 Hz).

(10) Selected spectral data for **5a**, ^{1}H NMR (CD$_2$Cl$_2$): δ 1.49 (m, 2H), 2.24 (s, 3H), 3.20 (m, 2H), 4.06−4.67 (m, 8H), 7.2−8.1 (m, 20H). ^{31}P NMR (CD$_2$Cl$_2$): δ 10.17 (d, J_{PP} = 15.5 Hz, J_{PPt} = 4764.5 Hz), 30.71 (d, J_{PP} = 15.5 Hz, J_{PPt} = 1430.1 Hz). ^{13}C NMR (CD$_2$Cl$_2$): $\delta_{(CO)}$ 244.0 (dd, J_{CP} = 13.4, 5.4 Hz).

(11) Selected spectral data for **6**, ^{31}P NMR (CD$_2$Cl$_2$): δ 18.46 (d, J_{PP} = 14.9 Hz, J_{PPt} = 4613.4 Hz), 21.55 (d, J_{PP} = 14.9 Hz, J_{PPt} = 1711.9 Hz).

(12) Pt(H)(Cl)(dppf) was generated in situ by the reaction of Pt(H)(Cl)(PPh$_3$)$_2$ with DPPF.

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JA0361042