1,4-Dihydroxylation of 1,3-Conjugated Dienes Promoted by the Pt(III) Dinuclear Complex

Masahiko Ochiai and Kazuko Matsumoto*
Department of Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

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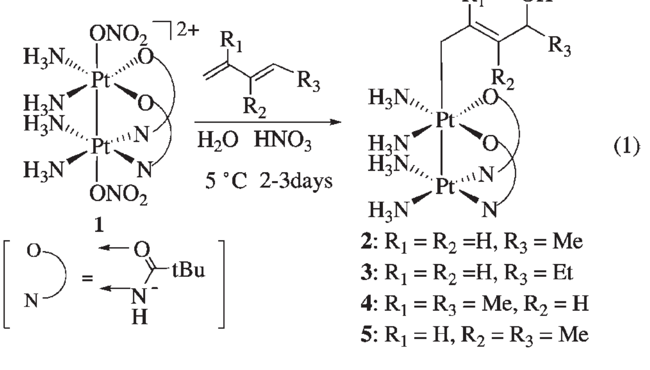
The pivalamidate bridged platinum(III) dinuclear complex reacted with various linear 1,3-conjugated dienes in water to give the 4-hydroxy-(*E*)-2-alkenyl-Pt(III) dinuclear complexes. The α-carbon atom of the axial alkenyl ligand bound to the Pt(III) atom is electrophilic and is easily attacked by solvent water to release (*E*)-2-alkene-1,4-diol exclusively.

The complexes of the general formula $[\mathrm{Pt^{III}}_2(\mathrm{NH_3})_4\mathrm{L_2L'L''}]^{n+}$, 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 give $[\mathrm{Pt^{II}}_2(\mathrm{NH_3})_4\mathrm{L_2}]^{2+}$ on reduction.[1–3] The axial ligands L' and L'' reversibly coordinate to the Pt atom in the redox reaction, whereas the rest of the structure is retained. These features make the compounds unique catalysts for selective oxidation of various alkenes.[4–6] In our previous study on the reaction of $[\mathrm{Pt^{III}}_2(\mathrm{NH_3})_4\mathrm{L_2L'L''}]^{n+}$ with olefins in water, the β-hydroxyalkyl-Pt(III)$_2$ complexes were isolated, which then released ketones, aldehydes, epoxides, and 1,2-diols by water attack.[5,6] For 1,2-dihydroxylation of monoolefins, Sharpless asymmetric dihydroxylation reaction using osmium compounds is well-known.[7,8] For 1,3-conjugated dienes, 1,2-diols are usually formed,[9,10] and 1,4-dihydroxylation is rarely observed. In the present reaction of $[\mathrm{Pt^{III}}_2(\mathrm{NH_3})_4((\mathrm{CH_3})_3\mathrm{CCONH})_2(\mathrm{NO_3})_2]^{2+}$ (**1**)[5] with 1,3-conjugated dienes, novel selective 1,4-diol formation was found.

Addition of linear 1,3-conjugated dienes **a-d** $\mathrm{CH_2 = CR^1\text{-}CR^2 = CH\text{-}R^3}$ (**a**, $R^1 = R^2 = H$, $R^3 = Me$; **b**, $R^1 = R^2 = H$, $R^3 = Et$; **c**, $R^1 = R^3 = Me$, $R^2 = H$; and **d**, $R^1 = H$, $R^2 = R^3 = Me$) to an aqueous solution of the Pt(III) dinuclear complex **1**, smoothly gave the corresponding 4-hydroxy-(*E*)-2-alkenyl-Pt(III) complexes $[\mathrm{Pt^{III}}_2(\mathrm{NH_3})_4((\mathrm{CH_3})_3\mathrm{CCONH})_2(\mathrm{CH_2CR^1 = CR^2CH(OH)R^3})]\,(\mathrm{NO_3})_3$ as represented in eq 1. All of the complexes obtained were identified by elemental analyses, ^{1}H NMR spectra, and X-ray diffraction analyses.[11–18] The X-ray structure of **4** is shown in Figure 1. The structural parameters of **2–5** are shown in Table 1.



(1)

1

2: $R_1 = R_2 = H$, $R_3 = Me$
3: $R_1 = R_2 = H$, $R_3 = Et$
4: $R_1 = R_3 = Me$, $R_2 = H$
5: $R_1 = H$, $R_2 = R_3 = Me$

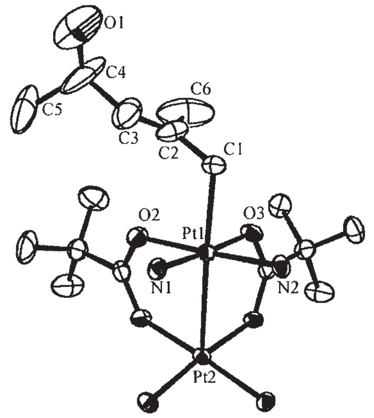


Figure 1. Structure of complex cation **4**.

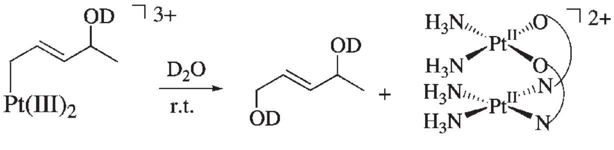
Table 1. Selected structural parameters of **2–5**

	2	3	4	5
Bond distances (Å)				
Pt1-Pt2	2.7337(8)	2.7351(7)	2.7403(8)	2.7318(8)
Pt1-C1	2.122(13)	2.056(13)	2.138(10)	2.114(12)
C1-C2	1.37(3)	1.443(17)	1.389(17)	1.42(2)
C2-C3	1.14(3)	1.176(16)	1.30(2)	1.27(2)
C3-C4	1.47(4)	1.60(2)	1.49(3)	1.38(6)
C4-O1	1.53(2)	1.58(2)	1.31(4)	1.41(5)
Bond angles (deg)				
C1-C2-C3	146(4)	135(3)	123.8(16)	130(2)
C2-C3-C4	141(4)	114(3)	126(3)	133(5)
C3-C4-C5	110(2)	100(3)	100(3)	115(4)
C3-C4-O1	105(3)	82(3)	110(3)	123(4)
C1-C2-C6			112.8(18)	
C6-C2-C3			123.1(19)	
C2-C3-C6				121(3)
C6-C3-C4				106(5)
Torsion angles (deg)				
C1-C2-C3-C4	−173(3)	−165(3)	176.5(18)	−175(4)
C4-C3-C2-C6			3(3)	
C1-C2-C3-C6				13(4)

The C2-C3 bond distances for all of the complexes are assigned to C=C double bonds. As for the complexes **2** and **3**, the distances are a little too short, but the bond angles of C1-C2-C3 and C2-C3-C4, and the torsion angles of C1-C2-C3-C4 suggest that the C2-C3 bonds are double bonds. The ^{1}H NMR spectra of these complexes also show the olefinic protons.[11,12]

In the ^{1}H NMR spectrum of the reaction solution of **1** with 1,3-pentadiene in D_2O, formation of **2** was observed after 5 min. The signals of the axial alkenyl ligand gradually decreased and the signals of the released (*E*)-2-pentene-1,4-diol[19] appeared after

1.5 h. The axial ligand was completely converted to (*E*)-2-pentene-1,4-diol after 24 h. In the last step of the 1,4-dihydroxylation reaction, the Pt(III) dinuclear complex was reduced to the corresponding Pt(II) dinuclear complex $[Pt^{II}_2(NH_3)_4((CH_3)_3CCONH)_2]^{2+}$ (**6**)[5] (eq 2).

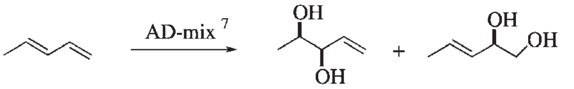


(2)

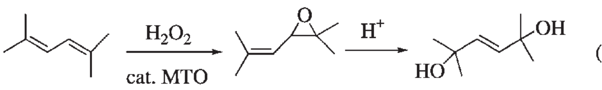
2 **6**

No signal other than **2**, **6**, and (*E*)-2-pentene-1,4-diol was observed during the conversion reaction. The same results were obtained in the reactions with **b**,[20] **c**, and **d**.[21]

Several dihydroxylation or epoxidation of 1,3-conjugated dienes are known,[9,22] in which 1,2-diols (eq 3) or ene-epoxides are obtained as the major products. Ene-1,4-diols are obtained only as minor products in the reaction of internal dienes via ene-epoxides (eq 4). In contrast, (*E*)-2-alkene-1,4-diols are exclusively obtained from terminal 1,3-dienes in the present reactions.



(3)[9]



(4)[22]

If the Pt^{II} dinuclear complex **6** can be re-oxidized to **1**, catalytic production of the 1,4-diols is possible.[23]

The present paper is dedicated to Prof. Teruaki Mukaiyama in the appreciation of his great contribution to Japanese organic chemistry and *Chem. Lett.*

References and Notes

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11 Complex **2**, Yield: 68%. Anal. Calcd for $[Pt_2(NH_3)_4(t\text{-}BuCONH)_2(C_5H_9O)](NO_3)_3(H_2O)$: C, 19.01; H, 4.57; N, 13.30%. Found: C, 19.06; H, 4.41; N, 12.64. ^{1}H NMR (270 MHz, D_2O): δ 7.07 (dd, $J = 15.12$, 5.94 Hz, 1H, CHC*H*CH(OH)), 6.16 (dt, $J = 15.39$, 7.83 Hz, 1H, CH_2CHCH), 5.17 (m, $J_{PtH} = 77.0$ Hz, 2H, $PtCH_2CH$), 3.84 (m, 1H, CHC*H*(OH)CH_3), 1.29 (d, $J = 6.75$ Hz, 3H, CH(OH)CH_3).
12 Complex **3**, Yield: 52%. Anal. Calcd for $[Pt_2(NH_3)_4(t\text{-}BuCONH)_2(C_6H_{11}O)](NO_3)_3$: C, 20.36; H, 4.59; N, 13.36%. Found: C, 20.11; H, 4.06; N, 13.02%. ^{1}H NMR (270 MHz, D_2O): δ 7.07 (dd, $J = 15.39$, 5.67 Hz, 1H, CHC*H*CH(OH)), 6.18 (dt, $J = 15.12$, 7.56 Hz, 1H, CH_2CHCH), 5.18 (m, $J_{PtH} = 77.5$ Hz, 2H, $PtCH_2CH$), 3.57 (m, 1H, CHC*H*(OH)CH_2), 1.62 (dq, $J = 13.8$ Hz, 7.29 Hz, 2H, CH(OH)CH_2CH_3), 0.95 (t, $J = 7.29$ Hz, 3H, CH_2CH_3).
13 Complex **4**, Yield: 63%. Anal. Calcd for $[Pt_2(NH_3)_4(t\text{-}BuCONH)_2(C_6H_{11}O)](NO_3)_3(H_2O)_2$: C, 19.61; H, 4.84; N, 12.87%. Found: C, 19.96; H, 4.42; N, 12.68%. ^{1}H NMR (270 MHz, D_2O): δ 6.84 (d, $J = 8.1$ Hz, 1H, CC*H*CH(OH)), 5.15 (m, $J_{PtH} = 75.3$ Hz, 2H, $PtCH_2$), 4.40 (m, 1H, CHC*H*(OH)CH_3), 2.21 (s, 3H, CH_2CCH_3), 1.33 (d, $J = 8.64$ Hz, CH(OH)CH_3).
14 Complex **5**, Yield: 55%. Anal. Calcd for $[Pt_2(NH_3)_4(t\text{-}BuCONH)_2(C_6H_{11}O)](NO_3)_3(H_2O)$: C, 19.98; H, 4.72; N, 13.11%. Found: C, 20.17; H, 4.67; N, 12.35%. ^{1}H NMR (270 MHz, D_2O): δ 6.01 (t, $J = 10.53$ Hz, 1H, CH_2CHC), 5.33 (m, $J_{PtH} = 78.6$ Hz, 2H, $PtCH_2CH$), 3.81 (q, $J = 7.02$ Hz, 1H, CC*H*(OH)CH_3), 1.33 (d, $J = 6.75$ Hz, 3H, CH(OH)CH_3), 1.07 (s, 3H, $CHCCH_3$).
15 Crystal data for **2**: $C_{15}H_{41}N_9O_{12}Pt_2$, fw = 929.75, yellow plate, monoclinic, space group $P2_1/c$ $a = 9.983(2)$, $b = 31.072(7)$, $c = 9.533(2)$ Å, $\beta = 95.631(4)$ deg, $V = 2942.8(12)$ Å^3, $Z = 4$, $d_{calc} = 2.099$ g cm^{-3}, $\mu = 9.564$ mm^{-1}, $R_1 = 0.0494$; $wR_2 = 0.1273$ for 4224 reflections ($F_o^2 > 2\sigma(F_o^2)$), $R_1 = 0.0595$; $wR_2 = 0.1328$ for all 13174 reflections.
16 Crystal data for **3**: $C_{16}H_{43}N_9O_{12}Pt_2$, fw = 943.77, yellow plate, monoclinic, space group $P2_1/c$ $a = 10.0780(14)$, $b = 31.710(4)$, $c = 9.5963(13)$ Å, $\beta = 94.911(3)$ deg, $V = 3055.5(7)$ Å^3, $Z = 4$, $d_{calc} = 2.052$ g cm^{-3}, $\mu = 9.213$ mm^{-1}, $R_1 = 0.0534$; $wR_2 = 0.1182$ for 6859 reflections ($F_o^2 > 2\sigma(F_o^2)$), $R_1 = 0.1036$; $wR_2 = 0.1338$ for all 11817 reflections.
17 Crystal data for **4**: $C_{16}H_{43}N_9O_{12}Pt_2$, fw = 943.77, yellow plate, monoclinic, space group $P2_1/c$ $a = 10.047(3)$, $b = 31.713(10)$, $c = 9.588(3)$ Å, $\beta = 94.943(6)$ deg, $V = 3043.6(16)$ Å^3, $Z = 4$, $d_{calc} = 2.060$ g cm^{-3}, $\mu = 9.249$ mm^{-1}, $R_1 = 0.0524$; $wR_2 = 0.1233$ for 6782 reflections ($F_o^2 > 2\sigma(F_o^2)$), $R_1 = 0.0724$; $wR_2 = 0.1331$ for all 18540 reflections.
18 Crystal data for **5**: $C_{16}H_{43}N_9O_{12}Pt_2$, fw = 943.77, yellow plate, monoclinic, space group $P2_1/c$ $a = 9.972(2)$, $b = 32.274(7)$, $c = 9.5687(19)$ Å, $\beta = 95.04(3)$ deg. $V = 3067.5(11)$ Å^3, $Z = 4$, $d_{calc} = 2.044$ g cm^{-3}, $\mu = 9.177$ mm^{-1}, $R_1 = 0.0553$; $wR_2 = 0.1350$ for 6765 reflections ($F_o^2 > 2\sigma(F_o^2)$), $R_1 = 0.0802$; $wR_2 = 0.1476$ for all 11817 reflections.
19 By comparison with the ^{1}H NMR spectrum of the authentic sample.; R. W. Bates, D. Díez-Martín, W. J. Kerr, J. G. Knight, S. V. Ley, and A. Sakellaridis, *Tetrahedron*, **46**, 4063 (1990).
20 By comparison with the ^{1}H NMR spectrum of the authentic sample.; K. Mori, M. Amaike, and H. Watanabe, *Liebigs Ann. Chem.*, **1993**, 1287.
21 The ^{1}H NMR spectra of the reaction solution with **c** and **d** showed the corresponding 1,4-diols as the major products.
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23 Such catalysis was attempted in the presence of 200 equiv of 1,3-pentadiene with several oxidizing reagents ($Na_2S_2O_8$, $Cu(NO_3)_2$, and $Ce(SO_4)_2$), pH (1–9), and the existence or absence of O_2, however turnover numbers of only less than 10 were obtained for 1 week reaction.