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Consecutive Double Nucleophilic Attacks on an Olefin Promoted by a Platinum(III) Dimeric Complex

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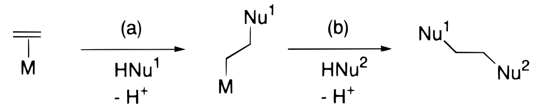
Summary: The double-nucleophilic attacks of methanol and water successively on the two carbon atoms of a double bond of olefins was realized on a Pt(III) dimeric complex to give the corresponding dinucleophile-substituted alkanes for the first time. Formation of the intermediate diplatinum(III) β-methoxy and β-hydroxyalkyl complexes was confirmed.

Nucleophilic attack is a useful fundamental process for introducing a nucleophile into an organic moiety often promoted by transition-metal complexes.[1] A transition-metal-coordinated olefin can be readily attacked by a nucleophile to form a metal−carbon bond, and the mechanism has been proved experimentally and theoretically (path a in Scheme 1).[1,2] On the other hand, 1,2-difunctionalization of olefins promoted by transition metals has been attempted as an important route in organic synthesis.[3] One plausible way to achieve such a reaction is 1,2-addition of two nucleophiles to a double bond as shown in Scheme 1. Cleavage of the metal−carbon bond in the alkyl−transition-metal intermediate via a second nucleophilic attack (path b in Scheme 1) is the key step yet to be realized. So far the metal−carbon bond is only cleaved oxidatively *in the presence of an oxidizing agent* to release the organic product containing two nucleophiles.[3,4] Diols have been synthesized from alkenes by employing oxometallic compounds, and the mechanism is somewhat different from the double-nucleophilic attacks.[5] Activation of the C−H bond in alkanes by a Pt(II)−Pt(IV) system to give alcohols has been postulated to involve the nucleophilic attack of water on a Pt(IV)−alkyl intermediate formed from the oxidation of the corresponding Pt(II)−alkyl complex by the Pt(IV) atom.[6,7]

Scheme 1



Nucleophilic attack at an olefin coordinated to the platinum(II) atom is well-known.[1] However, there have only been two olefin-coordinated platinum(IV) derivatives documented so far, whose reactivity is not known.[8] In our previous studies, olefin coordination to a platinum(III) atom was assumed as the initial step for the formation of alkyl−Pt(III) dinuclear complexes, in which intramolecular nucleophilic addition to the double bond was observed.[9] However, there has been no report to date on external nucleophilic attack at an olefin coordinated to Pt(III). In this paper, we report for the first time on the *consecutive double-nucleophilic attacks* of methanol and water on monoolefins promoted by a platinum(III) dimeric complex. The stereochemistry of the formation of 1,2-difunctional organic compounds is discussed.

Nucleophilic attack of methanol on the olefinic carbon undergoes smoothly by treatment of cyclopentene or cyclohexene with the pivalamidate-bridged Pt^{III}_2 complex $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(NO_3)_2](NO_3)_2$ (**1**), in methanol in the presence of $HClO_4$ to produce the β-methoxyalkyl−Pt(III) dinuclear complex $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(C_6H_{11}O)](ClO_4)_3 \cdot HClO_4$ (**2a**) or $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(C_7H_{13}O)](ClO_4)_3 \cdot HClO_4$ (**3a**), respectively, as represented in Scheme 2.[10] Analogous β-hydroxyalkyl−Pt(III) complexes, $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(C_5H_9O)](NO_3)_3$ (**2b**) and $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(C_6H_{11}O)](NO_3)_3$ (**3b**), were obtained in a similar manner by addition of olefins to an aqueous solution of **1** in the presence of HNO_3 (Scheme 2). The NMR studies confirmed the addition of R (R = OMe, OH) to the double bond and formation

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(10) In a typical experiment, complex **1** was prepared in situ by the oxidation of platinum blue complex $[Pt_4(NH_3)_8(C_5H_{10}NO)_4](NO_3)_5$ with $Na_2S_2O_8$ in the presence of $HClO_4$ in MeOH.[9] Addition of excess cyclopentene and stirring for 2 h at room temperature gave a pale yellow solution. Concentration followed by addition of H_2O gave the white complex **2a** (53%), which was identified by ^1H NMR and CHN elemental analysis. The elemental analysis indicates that both complexes **2a** and **3a** contain a molecule of $HClO_4$. The phenomenon of cocrystallization of acid in the isolation of diplatinum(III) complexes has been observed previously: Peilert, M.; Weissbach, S.; Freisinger, E.; Korsunsky, V. I.; Lippert, B. *Inorg. Chim. Acta* **1997**, *265*, 187. *Safety note*: Although we have not had any problem in using perchloric acid, the acid is known to be potentially explosive, especially when mixed with organic compounds and heated. Great caution should be exercised while handling it.

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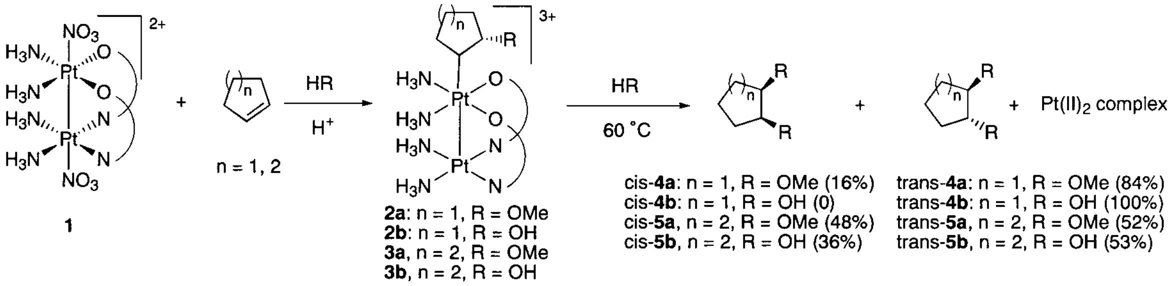
Scheme 2



1

n = 1, 2

2a: n = 1, R = OMe
2b: n = 1, R = OH
3a, n = 2, R = OMe
3b, n = 2, R = OH

cis-**4a**: n = 1, R = OMe (16%)
cis-**4b**: n = 1, R = OH (0)
cis-**5a**, n = 2, R = OMe (48%)
cis-**5b**, n = 2, R = OH (36%)

trans-**4a**: n = 1, R = OMe (84%)
trans-**4b**: n = 1, R = OH (100%)
trans-**5a**, n = 2, R = OMe (52%)
trans-**5b**, n = 2, R = OH (53%)

of a Pt^{III}–C bond.[11] Crystallographic analysis of complex **3b** shows that one of the two Pt(III) atoms and the OH group are mutually trans in the cyclohexyl ring (Figure 1), which clearly proves the exo addition (external attack) of the hydroxyl group to the double bond.[12]

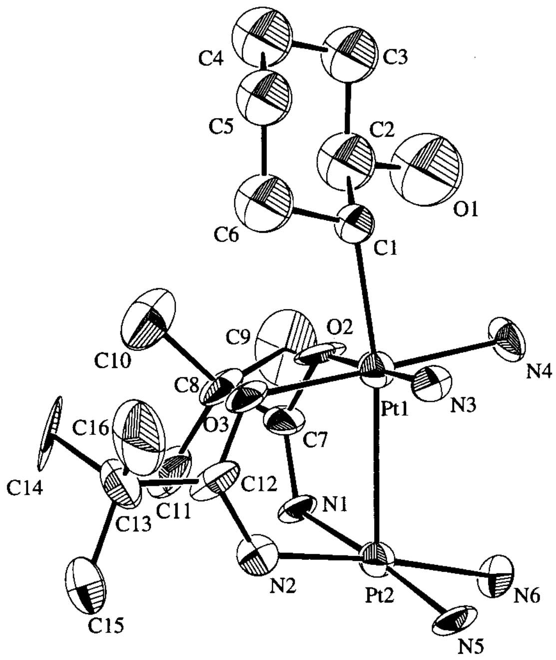


Figure 1. ORTEP drawing of complex **3b**. Thermal ellipsoids are drawn at the 30% probability level.

Of particular interest finding regarding the reactivity of these complexes is the achievement of the second nucleophilic attack at the α-carbon atom bonded to the Pt(III) atom *without any addition of oxidant*, as reported previously in the oxidative cleavage of a metal–carbon bond.[3,4] Thermal decomposition of **2a** in methanol under acidic conditions at 60 °C for 1 day releases *trans*-1,2-dimethoxycyclopentane (*trans*-**4a**) as the major product together with a small amount of cis isomer (*cis*-**4a**), as shown in Scheme 2.[13,14] In the same way, **3a** is decomposed to release the 1,2-addition products *trans*- and *cis*-1,2-dimethoxycyclohexane (*trans*- and *cis*-**5a**) in an approximately 1:1 molar ratio (Scheme 2).[13,14] The scrambling of the stereochemistry at the carbon atom in the decomposition of **3a** implies that different mechanisms are involved in the second nucleophilic attack. Formation of cis isomers of dimethyl ethers indicates trans nucleophilic attack of the second methanol molecule to the carbon atom bonded to the Pt(III). Hence, *cis*-1,2-difunctionalization of a monoolefin via the consecutive double trans nucleophilic attacks is realized on the platinum(III) dimeric complex. It is known that generally alkyl–transition-metal complexes tend to react with electrophiles, such as protic acids and halogens, to generate organic compounds.[1] The novel electrophilicity of the alkylplatinum(III) complex can be accounted for by the unusually high oxidation state of the Pt(III) atom with strong electron-withdrawing ability, which favors the nucleophilic attack and disfavors the protonation of the alkyl ligand, opposite to the normal metal–alkyl property. Nucleophilic attack of water is possible on the alkyl carbon atom bound to a Pt(IV),[6,7] but Pt(IV) is not usually coordinated by an olefin, except in the presence of a special ligand to stabilize the complex.[8] An electrophilic alkyl–Pt(II) complex is reported, but that is also an exceptional case and needs a strong electron-withdrawing group in the ligand.[15] A methyl–Hg(II) complex is also known to exhibit electrophilic properties,[16] but Hg(II) is not very reactive toward olefins. Considering these tendencies of the high-valent metals toward olefins and the reactivity of the metal alkyls, Pt(III) is a special metal that can be coordinated generally by olefins and its alkyl complexes can receive nucleophilic attack.

As for the mechanism of the production of *trans*-**4a** and *trans*-**5a**, substitution of one coordinated oxygen atom of the pivalamidate ligands by a molecule of methanol in the presence of acid can be proposed.[17] This should be followed by the attack of the coordinated alcohol on the alkyl α-carbon, eliminating trans dimethyl ether.

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[11] The two vicinal protons in the Pt–C*H*–C*H*–OR moiety give the characteristic signals in ^{1}H NMR in all four complexes **2a**,**b** and **3a**,**b**; i.e., a multiplet appears in the range of 4.5–4.8 ppm with two satellite signals having the coupling constants $^2J_{\mathrm{Pt-H}}$ in the range 65–70 Hz. Another multiplet at 3.5–3.9 ppm can be assigned to the proton atom linked to the C–OR moiety. A singlet around 3.4 ppm belongs to the protons of OMe group in complexes **2a** and **3a**.

[12] Crystal data for **3b** at 20 °C: triclinic, space group $P\bar{1}$, a = 10.367(3) Å, b = 14.873(5) Å, c = 9.770(4) Å, α = 92.28(3)°, β = 99.16(3)°, γ = 89.87(2)°, V = 1486.0(8) Å^3, Z = 2. The final discrepancy indices were R = 0.067 and R_w = 0.070. GOF = 1.34.

[13] The identification and configurational assignment of the released cis and trans isomers of the mono- and dimethyl ethers were achieved by GC-MS and the comparison of the ^{1}H NMR spectra with those of the independently synthesized ones as described in: Winkler, J.; Grützmacher, H.-F. *Org. Mass Spectrom.* **1970**, *3*, 1117.

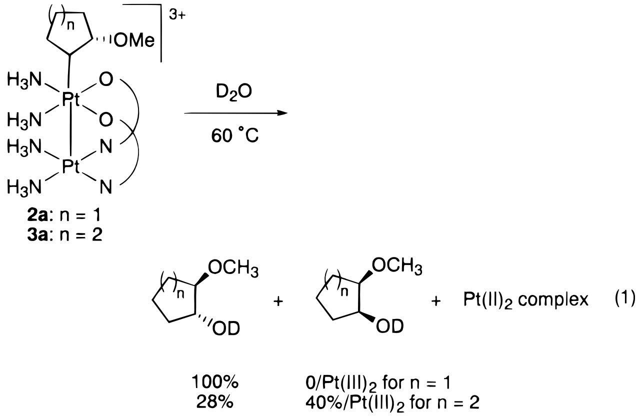
[14] Treatment of **2a** and **3a** with excess NaOMe in CD_3OD or NaOH in D_2O at ambient temperature gave 3-methoxy-1-cycloolefins along with trace amounts of cycloolefins and a small amount of unidentified products, indicating that β-H elimination is a predominant process over nucleophilic attack in the presence of base.

[15] Bennett, B. L.; Birnbaum, J.; Roddick, D. M. *Polyhedron* **1995**, *14*, 187.

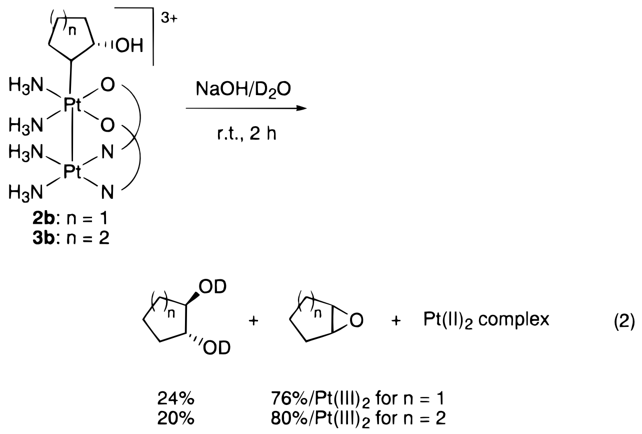
[16] Periana, R. A.; Taube, D. J.; Evitt, E. R.; Löffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340.

[17] Replacement of one of the two pivalamidate ligands rather than the coordinated NH_3 ligand was observed in the treatment of complex **1** with a concentrated aqueous solution of HCl.

The second attack of a nucleophile on complexes **2a** and **3a** was also observed in the solvolysis of the complexes in D_2O at 60 °C for 24 h (eq 1). Complex **2a** gave *trans*-1,2-cyclopentanediol monomethyl ether exclusively, whereas *cis*- and *trans*-1,2-cyclohexanediol monomethyl ether were yielded together with an unidentified compound when **3a** was decomposed in D_2O (eq 1).[13]



Evidence for the second nucleophilic attack can also be obtained by the thermal decomposition of **2b** and **3b**. A trans diol (*trans*-**4b**) is afforded as the unique product on heating **2b** in D_2O at 60 °C for 3 h (Scheme 2).[18] Both trans (*trans*-**5b**) and cis diols (*cis*-**5b**) were found in a 3:2 molar ratio together with a minor product cyclopentylcarbaldehyde (11%) in the decomposition of complex **3b** (Scheme 2).[19] However, addition of excess NaOH to the aqueous solutions of **2b** and **3b** at room temperature results in the formation of cycloolefin oxides as the major products along with trans diols as represented in eq 2. Clearly, the oxide formation indicates that intramolecular nucleophilic attack proceeds more rapidly than the external OH^- attack. Similar intramolecular nucleophilic attack has been observed in the treatment of $[Pt^{IV}Cl_5(CH_2CH_2OH)]^{2-}$ with excess NaOH to generate ethylene oxide.[20] The mechanism for *cis*-**5b** formation would be similar to that for cis dimethyl ether formation, consisting of trans nucleophilic attack of water at the coordinated cycloolefin to form **3b**, which then receives a second trans nucleophilic attack. For the formation of trans diols, there are two possible routes: one is the formation of oxide by intramolecular nucleophilic attack followed by hydrolysis, and the other is the substitution of an oxygen atom of the pivalamidate ligands by water and subsequent reductive elimination of diol as discussed above for the formation of trans dimethyl ethers. The comparison with the results of the methanol addition, however, suggests the latter route as a more plausible pathway for the trans diol formation by heating under acidic conditions.



It is worthy to note that the aforementioned first and second nucleophilic attacks can be achieved successively by preparing alkyl complexes in situ without isolation.

Consecutive double-nucleophilic attacks of methanol and water on a monoene under acidic conditions to give 1,2-addition organic products have been established as a new fundamental reaction in organometallic chemistry. This type of process is intriguing not only as fundamental chemistry but for the application in catalytic reactions, in which spontaneous cleavage of a metal−carbon bond is required. Employment of the new finding in Pt(III)-catalyzed reactions to synthesize 1,2-addition products is still in progress.

Supporting Information Available: Text and tables giving X-ray data for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The diols formed and their stereochemistry were confirmed by comparing the ^1H NMR spectra with those of standard samples.

(19) Formation of cyclopentylaldehyde can be explained in terms of a ring rearrangement with a carbonium ion mechanism; see: Byrd, J. E.; Cassar, L.; Eaton, P. E.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1971**, 40.

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