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Inorganic and organometallic chemistry of Pt^{III} complexes having a delocalized $Pt^{III}—Pt^{III}$ bond*

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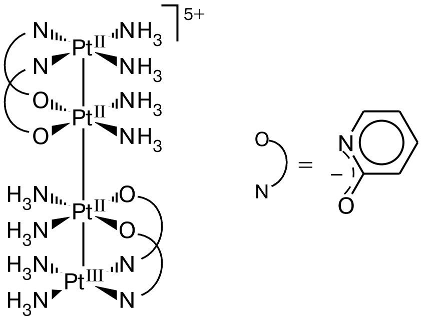
Amidate-bridged dinuclear Pt^{III} complexes having a $Pt^{III}—Pt^{III}$ bond react with ketones and alkenes. In the reaction with alkenes in water, 1,2-diols are obtained. In the reactions with conjugated dienes, stereospecific 1,4-diols are formed selectively. A kinetic study revealed that at each intermediate step of the reaction with alkenes the electronic state of the Pt—Pt bond changes between $Pt^{III}—Pt^{III}$ and $Pt^{II}—Pt^{IV}$ and stabilizes the reaction intermediates.

Key words: platinum(III), platinum—platinum bonds, olefin oxidation.

Platinum(III) is an unusual oxidation state and is isolated only in certain structures having special ligands for stabilization. The blue $Pt^{II,III}$ mixed-valent compounds of the general formula $[Pt_4(NH_3)_8L_4]^{5+}$ (L is deprotonated amidate ligand)[1] are a class of such stable Pt^{III} compounds (see the α-pyridonate-bridged blue platinum complex as example).



The blue compounds were found to consist of three Pt^{II} and one Pt^{III}, having one unpaired electron arising from Pt^{III}. Subsequent synthetic and electrochemical studies revealed that the platinum blues are reversibly oxidized or reduced between Pt^{III} dimers $[Pt(NH_3)_4L_2L'_2]^{2+}$ (L′ is uninegative axial ligands such as halide, nitrate or nitrite) and Pt^{II} dimers $[Pt(NH_3)_4L_2]^{2+}$, respectively (Scheme 1).[2—8]

The amidate-bridged dinuclear Pt^{III} complexes (see Scheme 1) always have axial ligands. Before our studies on the organometallic chemistry at the axial positions were undertaken, all of the axial ligands had been inorganic ones, such as water, nitrate, or halide. Therefore, the reaction of Pt^{III} with alkyls, alkenes, and alkynes was totally new, and it was worth studying the extent of the stability of a $Pt^{III}—C$ bond, and whether the alkyl group is susceptible toward nucleophilic attack or electrophilic attack.

In this paper, organometallic chemistry of amidate-bridged dinuclear Pt^{III} complexes at the axial positions is introduced. All of the organometallic chemistry of Pt^{III} has been studied in the author's group*, and unexpectedly high reactivity of Pt^{III} toward various unsaturated organic molecules has been observed.

Ketonylplatinum(III) dinuclear complexes

The first ketonyl-Pt^{III} dinuclear complex with pivalamide bridging ligands, $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2COCH_3)](NO_3)_3$ (**1**)[9,10]

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* Materials were presented at the Mark Vol'pin Memorial International Symposium "Modern Trends in Organometallic and Catalytic Chemistry" dedicated to his 80th anniversary.

* ^1H NMR spectra were recorded on a JEOL Lambda 270 spectrometer operating at 270 MHz. The chemical shifts were reported in ppm units downfield from Me_4Si. The X-ray diffraction intensities were collected on a Rigaku AFC-7R diffractometer or a Bruker Smart-CCD diffractometer by using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Preparation of ketonylplatinum(III) dinuclear complexes,[9,10] and other alkylplatinum(III) dinuclear complexes[11,12] were carried out according to the literatures. The kinetic study of the reactions of the $[(H_2O)(NH_3)_2PtL_2Pt(NH_3)_2(NO_3)](NO_3)_3 \cdot 2H_2O$ complex (L is μ-α-pyridonate)[13] with olefins was carried in 2.0 *M* $HClO_4$ containing $NaClO_4$ by using a rapid-scan/stopped-flow USP-500 scanning spectrometer (Unisoku Scientific Instruments) and UV-160A (Shimadzu), UV-2200 (Shimadzu), and US-2400 (Shimadzu) spectrophotometers. Rate constants were measured by monitoring the absorbance change in the UV region. The details of the experiment are given in Ref 14.

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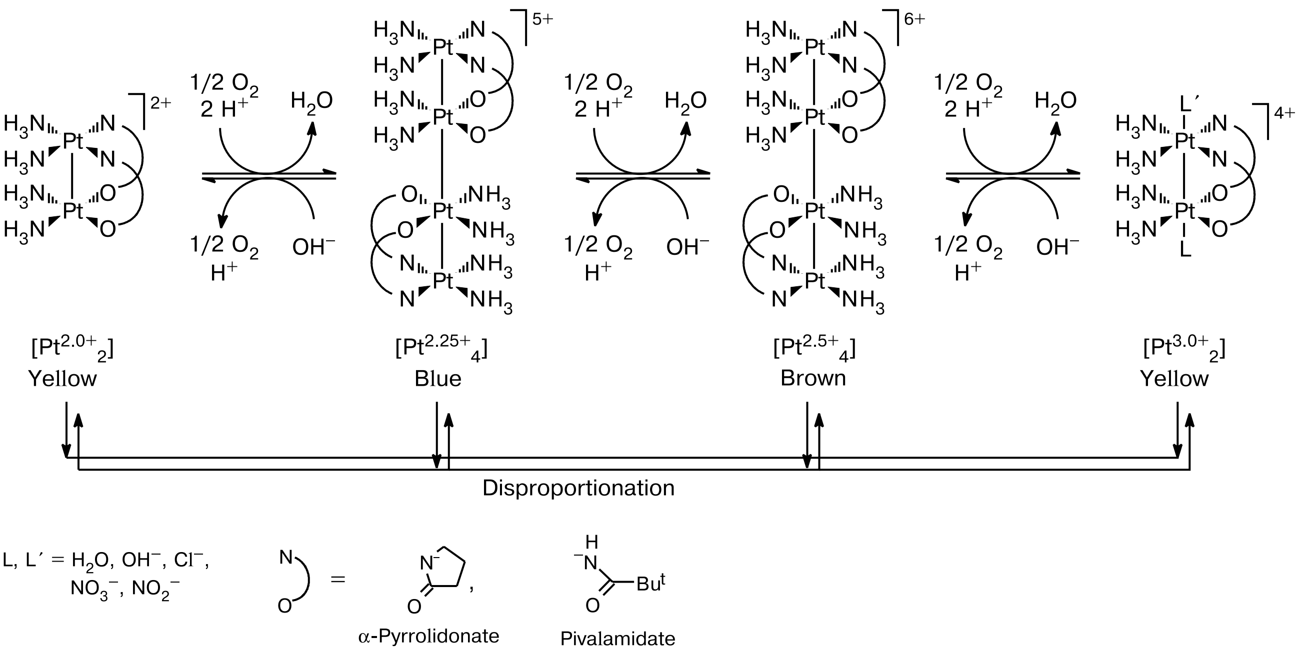
Scheme 1



was prepared by the reaction of the $Pt^{II,III}$ mixed-valent platinum blue complex $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ (**2**) with neat acetone in the presence of either HNO_3 or $Na_2S_2O_8$ as the oxidizing agent (Scheme 2).

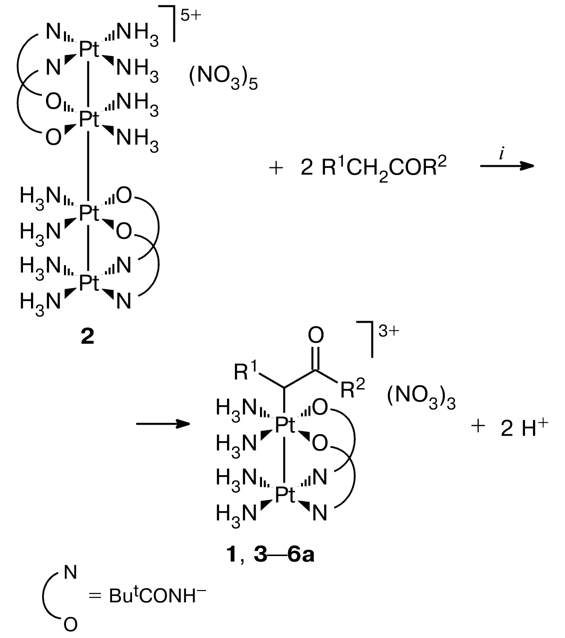
The acetonyl carbon is bound axially to one of the Pt^{III} atoms in complex **1**, while the other Pt^{III} atom has the nitrate as a weakly coordinated axial ligand (Fig. 1). In contrast to most alkyl-transition metal complexes, compound **1** was prepared in acidic aqueous solution.

Butanone having two different α-C—H bonds gave a mixture of two ketonyl-Pt^{III} complexes, namely $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH(Me)COMe)](NO_3)_3$ (**6b**) and $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2COEt)](NO_3)_3$ (**6c**), in a molar ratio of 1.7 : 1 (Scheme 3).

However, the reaction with 3-methylbut-2-anone afforded only one complex $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2COCHMe_2)](NO_3)_3$ (**6a**) exclusively as a result of α-Me group C—H bond activation (see Scheme 2).

The carbon atom bound directly to the Pt^{III} atom was found to undergo nucleophilic attack in water. For instance, the Pt^{III} dinuclear complex **1** reacts with water or NaOH and NaBr to release α-hydroxyacetone and α-bromoacetone, and complex **1** is reduced to the corresponding Pt^{II} dinuclear complex. Similarly, all of the ketonyl Pt^{III} complexes (see Scheme 2) react with water or NaOH and $HNEt_2$ to release the α-hydroxysubstituted and α-aminated ketones (Scheme 4).

Scheme 2



	R^1	R^2		R^1	R^2
1	H	Me	**5**	H	CH_2COMe
3	H	Ph	**6a**	H	$CHMe_2$
4	Me	Et			

i. Conc. HNO_3, ~20 °C.

An electrophilic alkyl-Pt^{II} complex has been reported as an exceptional case, in which a strong electron-withdrawing group is attached to the ligand.[15] A methyl-Hg^{II} complex is also known to exhibit electrophilic proper-

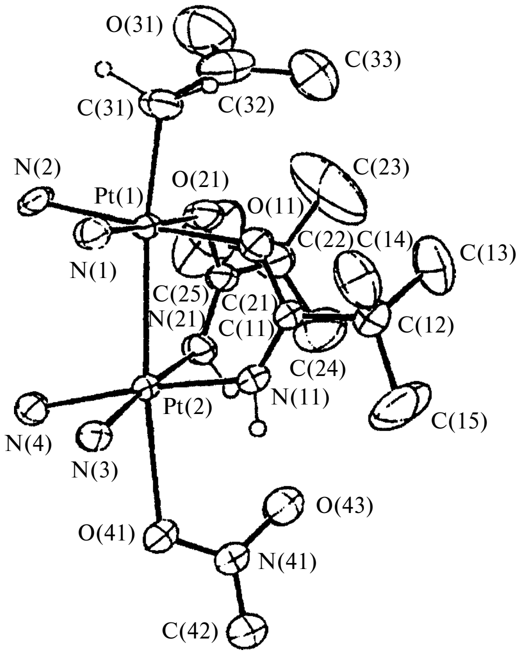
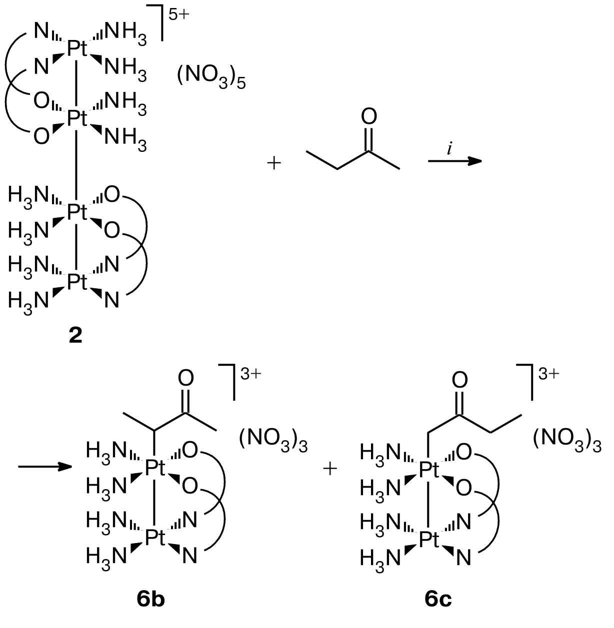


Fig. 1. Molecular structure of the $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2COMe)(NO_3)]^{2+}$ complex (**1**).

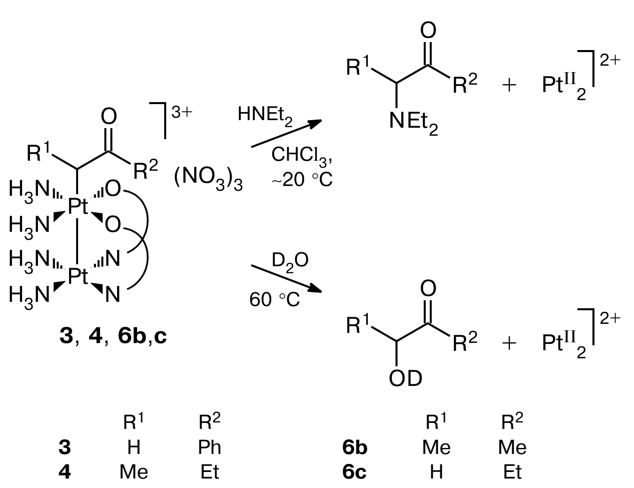
Scheme 3



i. Conc. HNO_3, –20 °C.

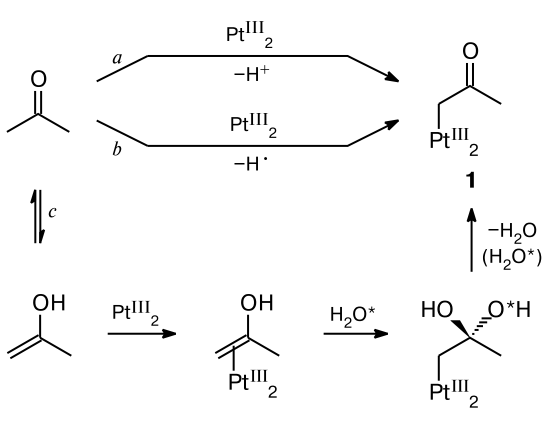
ties.[16] Except for these few rare cases, electrophilic alkylmetal complexes are rare, and in this sense, Pt^{III} complexes are valuable.

Scheme 4



Formation of a number of ketonyl transition metal complexes is reported to proceed *via* (i) reaction of ketone with a hydroxyl complex or a complex having a basic ligand, (ii) reaction of ketone with a low-valent transition metal complex in the presence of a base, and (iii) oxidative addition of chloroketone or an α-C—H bond of ketone to a low-valent transition metal complex.[17—29] It is noteworthy that, in contrast to these mechanisms, complex **1** is prepared in strongly acidic aqueous solution. In the C—H bond activation of acetone with platinum blue complexes, the platinum(III) dinuclear complex $[Pt_2(NH_3)_4(Bu^tCONH)_2(H_2O)_2](NO_3)_4$ (**7**) has been shown to be the active species. In fact, complex **1** can be prepared also from previously isolated complex **7**,[11,23] and, therefore, oxidative addition of acetone to the mixed-valent lower oxidation state is excluded as the possible formation mechanism for complex **1**. For the C—H activation of acetone, the three routes shown in Scheme 5 can be conceived as the reaction path.

Scheme 5



Route *a* is an electrophilic displacement of H^+ in acetone by the electrophilic Pt^{III} atom. Homolytic cleavage of the C—H bond forming an acetonylplatinum(III) complex is another pathway (route *b*). In the third possibility shown as route *c*, the double bond of the enol form of acetone is coordinated to the Pt^{III} atom, and then nucleophilic attack of water takes place to eliminate one H_2O molecule. The nucleophilic attack on the double bond of alkenes coordinated to the platinum(III) dimeric complex really occurs and is discussed in the next section. The synthetic and NMR experiment of the reactions using $H_2{}^{18}O$, and the use of radical trapping reagent excluded the possibility of routes *b* and *c*, and, therefore, route *a*, electrophilic replacement, seems to be the most probable route.[10]

Olefin oxidation catalyzed by amidate-bridged Pt^{III} dinuclear complexes

The amidate-bridged Pt^{III} dinuclear complexes are reduced to the corresponding Pt^{II} dinuclear complexes by OH^-, and the latters are reoxidized to the Pt^{III} dinuclear complexes by molecular oxygen (see Scheme 1). The axial ligand on the Pt^{III} is released on reduction to the Pt^{II} dinuclear complex. Since these features seem suitable for oxidation catalysis, olefin oxidation was attempted by using air or O_2 as the oxidant and the α-pyrrolidonate-bridged platinum tan compound $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ (**8**) or pivalamidate-bridged platinum blue compound **2** as the catalyst in the acidic $H_2O—CH_2ClCH_2Cl$ biphasic solution.[11,23] In a typical experiment, 10 μmoles of the Pt complex and a 5—6-fold equivalent amount of the phase transfer agent, $C_{12}H_{25}SO_3Na$ were dissolved in a mixture of 1 mL of 0.05 *M* H_2SO_4 and 1 mL of CH_2ClCH_2Cl containing a 400-fold equivalent amount of olefin. The reaction was carried out in an O_2 atmosphere at 50 °C for 5 days. The result is shown in Table 1. Linear terminal olefins are selectively oxidized to alkan-2-ones, whereas cyclic olefins (cyclohexene and norbornene) are selectively oxidized to epoxides. The linear internal olefin oct-2-ene is oxidized to both octan-2-one and octan-3-ones.

Although the oxygen atom in the products has been expected to come from the atmosphere, mass analysis of the products showed that all of the oxygen atoms in the products originate from the solvent water. The reaction was also carried out under $^{16}O_2$ in $D_2{}^{16}O$, and it was confirmed that deuterium was not present in the products. The true catalyst was also confirmed to be the Pt^{III} dinuclear complexes, $[Pt_2(NH_3)_4(C_4H_6NO)_2(H_2O)_2]^{4+}$ (**9**) and **7**.[23] From these facts, it was conceived that the reaction mechanism is similar to the Wacker process (see Scheme 6). In all the entries in Table 1, the turnover numbers are not high, but this is not because the catalyst is disrupted, as confirmed by the fact that addition of the oxidizing agent $Na_2S_2O_8$ to oxidize the Pt^{II} dimer to the Pt^{III} dimer regenerated the catalyst. However, addition of $Na_2S_2O_8$ from the beginning of the reaction hindered the reaction. It seems that the oxidation reaction rate is not high enough under the catalysis condition, and the platinum reduced form gradually accumulates in the solution.

Table 1. Olefin oxidation catalyzed by the blue platinum complexes

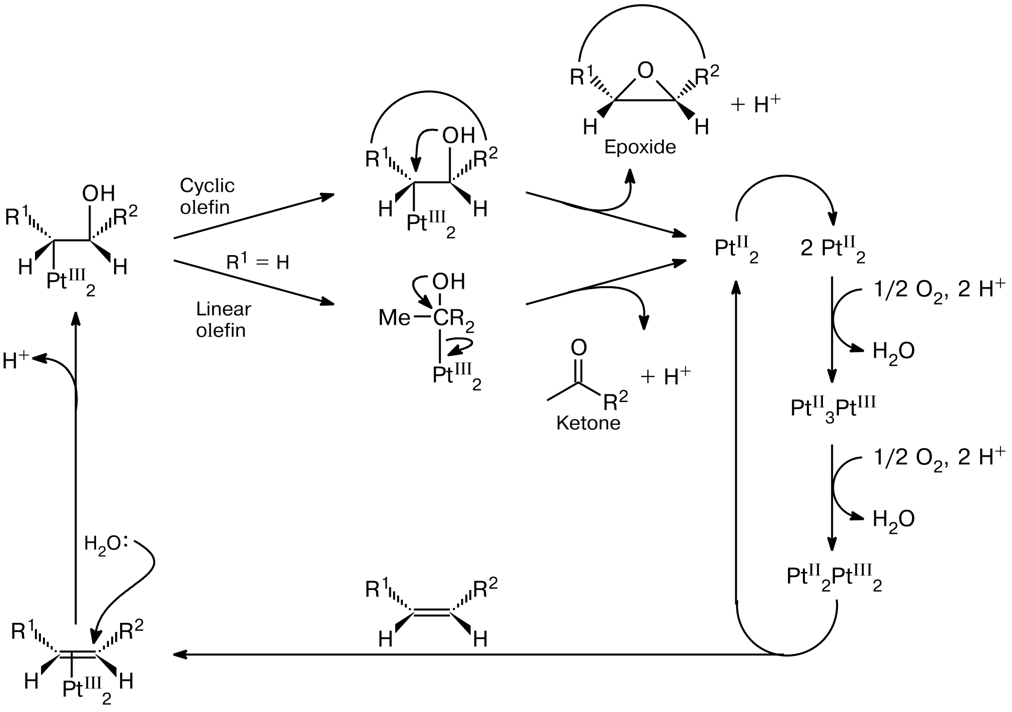
Substrate	Product	Turnover number[a]	
		complex **8**	complex **9**
Hex-1-ene	Hexan-2-one	11.9	3.8
	1,2-Epoxyhexane	8.6	8.8
Hept-1-ene	Heptan-2-one[b]	13.3	4.5
Oct-1-ene	Octan-2-one[b]	15.8	12.4
Dec-1-ene	Decan-2-one	10.9	4.1
Oct-2-ene	Octan-2-one	1.7	1.6
	Octan-3-one	2.2	1.6
Cyclohexene	Epoxycyclohexane	22.8	15.0
	Cyclohexanone[c]	1.9	1.4
Cyclopentene	Cyclopentanone	2.0	2.5
Norbornene	Epoxynorbornane	7.2	5.2
	Norbornane[d]	2.3	0.6
2-Methylbut-2-ene	3-Methylbutan-2-one	—	—
Ethyl vinyl ether	Acetaldehyde	—	—
	Ethanol	—	—
1-Chloroprop-1-ene	—	No reaction	
1-Bromoprop-1-ene	—	No reaction	
α-Methylstyrene	—	No reaction	
β-Methylstyrene	—	No reaction	
Allylbenzene	—	No reaction	

[a] The turnover number is equal to the ratio of concentrations of the product to complex.
[b] The minor product (<1%) is 1,2-epoxide.
[c] The minor product (<1%) is cyclopentanecarbaldehyde.
[d] The minor product (<1%) is norborneol.

Alkylplatinum(III) dinuclear complexes prepared from alkenes

The proposed reaction mechanism for olefin oxidation (see Scheme 6) suggests that olefins π-coordinate axially to Pt^{III}. If so, it is very scientifically meaningful, since Pt^{II} coordinates olefins in the equatorial plane, whereas Pt^{IV} does not coordinate olefins, except in a special complex. Isolation of Pt^{III}-olefin complexes would be the first proof of the olefin coordination in the Pt^{III} chemistry. If the mechanism proposed (see Scheme 5) is correct, it also shows that 1,2-shift occurs on Pt^{III} similar to Pt^{II}, and the carbon atom on the Pt^{III} undergoes nucleophilic attack. If these are proved, they would construct the fundamental chemistry of Pt^{III}. Attempts to isolate the Pt^{III} π-complex were unfortunately not successful either in aqueous or organic solvent. However,

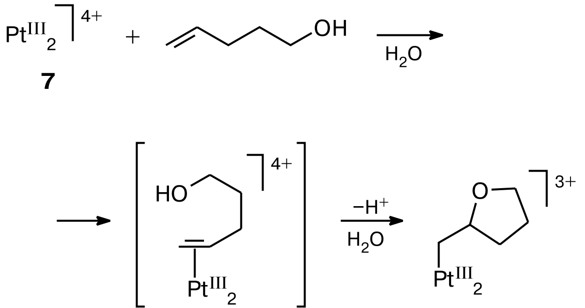
Scheme 6



alkyl Pt^{III} complexes were unexpectedly obtained. Their structures and solution behavior indicate the typical nature of Pt^{III} as explained below.

Isolation of the reaction products with simple monoolefins was at first not easy, and the first product obtained was with hydroxyl-substituted olefins as shown in Schemes 7 and 8.[11]

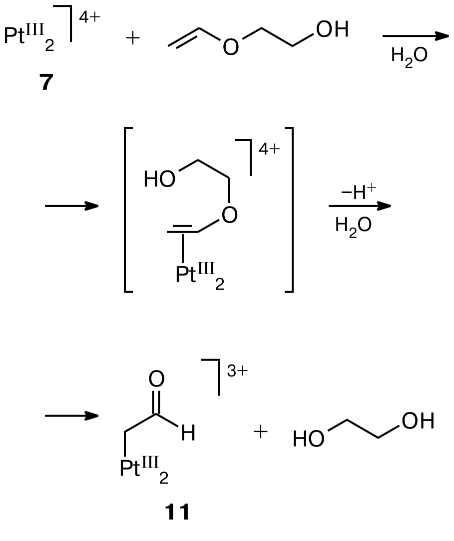
Scheme 7



The structures of the products $[Pt^{III}_2(NH_3)_4(Bu^tCONH)_2(CH_2CH(CH_2)_3O)](NO_3)_3 \cdot H_2O$ (**10**) and $[Pt^{III}_2(NH_3)_4(Bu^tCONH)_2(CH_2CHO)](NO_3)_3 \cdot \cdot H_2O$ (**11**) are shown in Figs. 2 and 3.

In most of the alkyl Pt^{III} complexes, the axial *trans*-position to the alkyl group *via* the $Pt^{III}—Pt^{III}$ bond is vacant owing to the large trans-effect of the alkyl group. In the

Scheme 8



acetonyl complex (see Fig. 1), the Pt_{trans}—O (nitrate) distance is unusually long (2.667(7) Å). The bond distances of the alkyl group of complex **11** are shown in Fig. 4, which shows that the actual electronic structure is intermediate between the σ-ketonyl complex and the π-olefin complex.

Complex **10** is stable in acidic to weakly basic aqueous solution. However, upon addition of 0.1 *M* NaOH, the nucleophilic attack occurs at the β-carbon (Scheme 9).

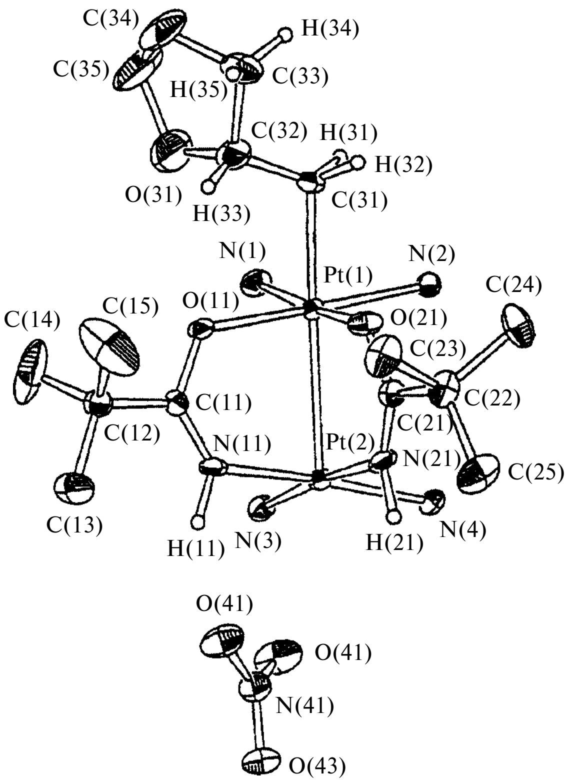


Fig. 2. Molecular structure of the $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2\overline{CH(CH_2)_3O})](NO_3)_3\cdot 3H_2O$ complex (**10**).

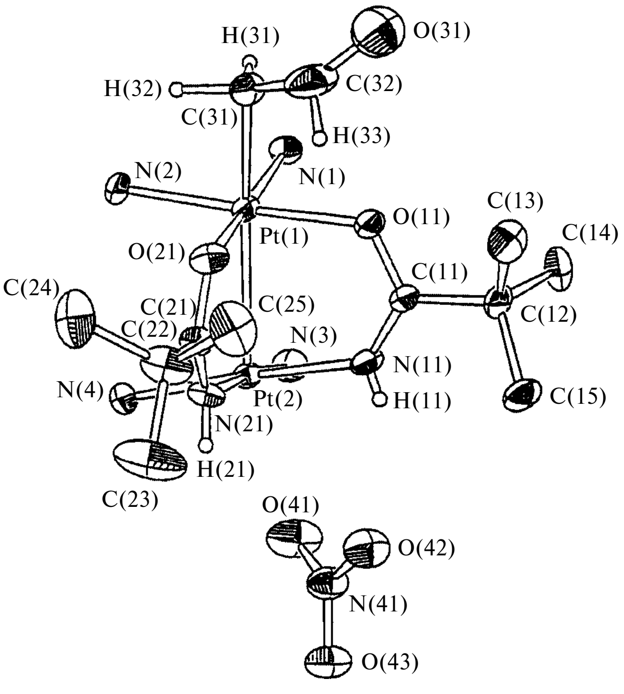


Fig. 3. Molecular structure of the $[Pt_2(NH_3)_4(Bu^tCONH)_2(CH_2CHO)](NO_3)_3\cdot H_2O$ complex (**11**).

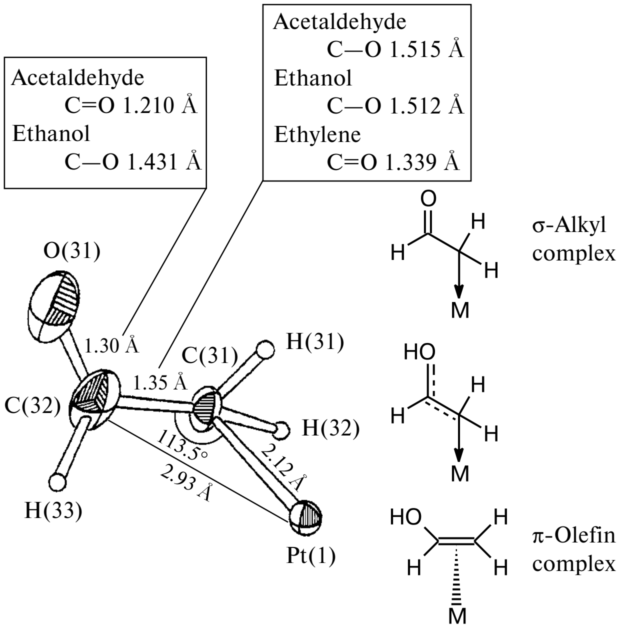
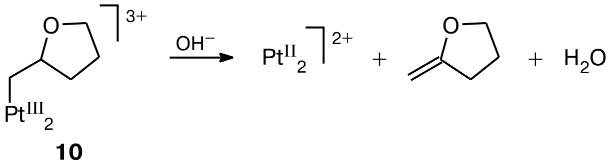


Fig. 4. Structure of the β-hydroxyethyl group in complex **11**.

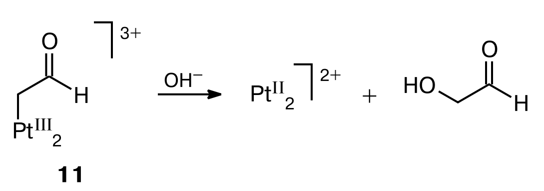
The reaction may also be considered to proceed *via* initial α-hydroxylation, which eventually leads to dehydration to give the product.

Scheme 9



Complex **11** is unstable at room temperature even as a solid and is easily hydrolyzed in neutral aqueous solution to produce glycol aldehyde (Scheme 10). In 0.1 *M* $HClO_4$ complex **11** produces glycol aldehyde and acetic acid in a ratio close to 9 : 1.

Scheme 10



The ^1H NMR spectrum of complex **11** in D_2O is shown in Fig. 5. Different from what is expected for the crystal structure of complex **11**, two sets of signals (σ and π) are observed, whose relative intensities reversibly vary depending on the pH. These peaks are assigned as the acid-

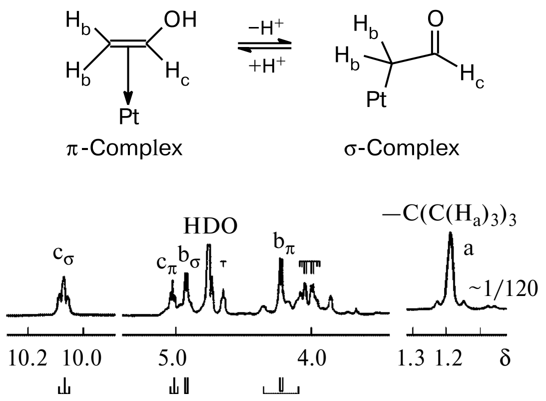


Fig. 5. ^1H NMR spectrum of a solution of complex **11** in D_2O. Protons of the $—C(C(H_a)_3)_3$ group correspond to protons of pivalamidate-bridged ligands. Small peaks at δ 4.0 and 4.6 can probably be assigned to the decomposition products.

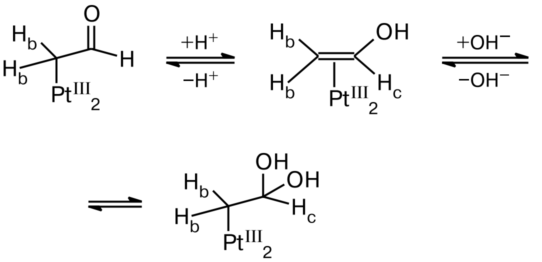
Table 2. Data of ^1H NMR spectroscopy for a solution of complex **11** in D_2O

Complex	δ			$^3J_{H_b,H_c}$	$^2J_{Pt,H_c}$
	H_a	H_b	H_c	Hz	
π-Complex	1.18	4.19	5.01	4.3	69
σ-Complex	1.17	4.88	10.05	4.3	—

base equilibrium between the π-vinyl alcohol and β-oxoethyl structures as shown in Fig. 5.

The ^1H chemical shifts of compound **11** are listed in Table 2. The assignment of peaks was confirmed by the ^1H-^1H COSY spectrum. A similar acid-base equilibrium between π- and σ-complexes is reported for the vinyl alcohol-Pt^{II} complex in acetone,[24—26] in which, however, the two forms do not give separate signals and appear at an intermediate chemical shift between those of the two forms. In both of the Pt^{II} and the present Pt^{III} compounds, the two H_b protons are equivalent, giving only a doublet for these protons and a triplet signal for the H_c proton. The spectrum of the π-complex **11** is the A_2X pattern, although from the X-ray structure, it is expected to be ABX. A similar A_2X pattern is also observed in the vinyl alcohol π-complex of Pt^{II} in acetone.[24,25,27] The reason for the A_2X pattern in complex **11** is probably as follows. The π-complex **11** is in equilibrium with the dihydroxyethyl form, and exchange between the two forms is rapid (Scheme 11).

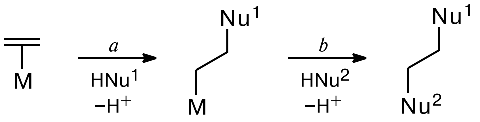
Scheme 11



Dihydroxylation of monoolefins and dienes with the Pt^{III} dinuclear complexes

The previous section describes nucleophilic attack of the α-carbon atom on the dinuclear Pt^{III} complex, indicating that consecutive dinucleophile addition can be achieved onto alkenes as shown in Scheme 12. Such consecutive double nucleophilic attack had not been realized on any metal.

Scheme 12

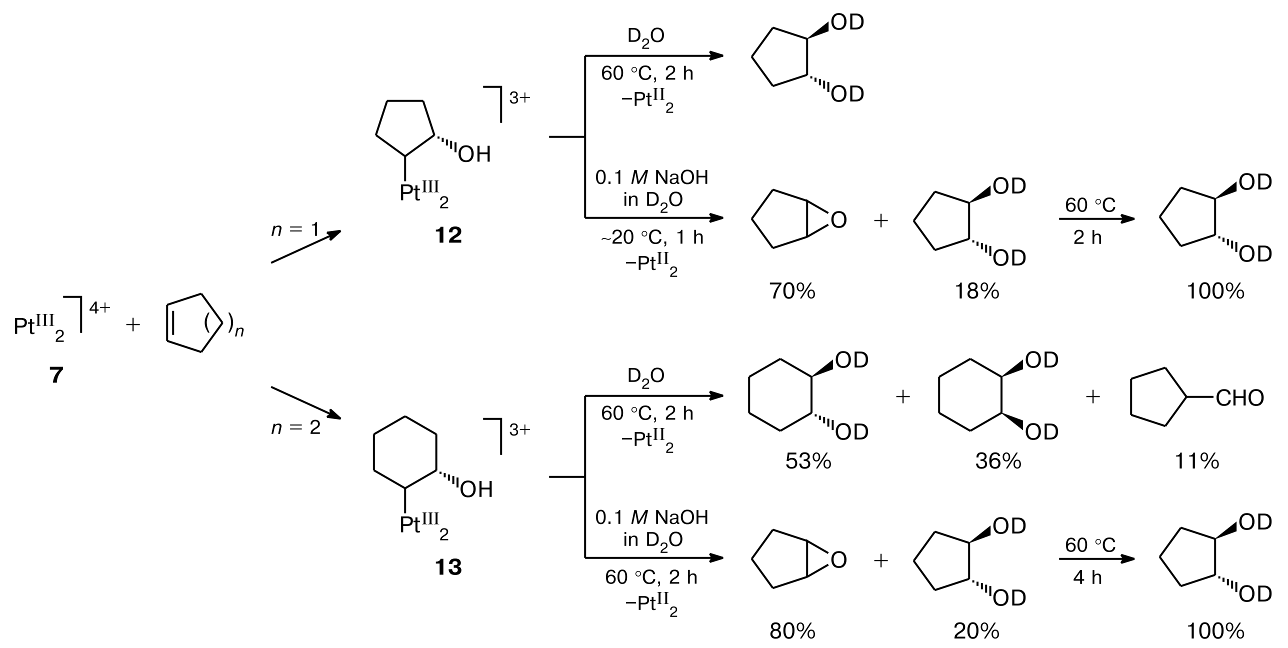


The reaction of the pivalamidate-bridged Pt^{III} dinuclear complex **7** with cyclic monoolefins gave 1,2-disubstituted cyclic alkanes as expected (Scheme 13).[12] Interestingly, the β-hydroxy cyclohexyl complex was isolated as an intermediate, and the crystal structure clearly shows that the hydroxylation occurs by *trans*-addition (Fig. 6). The dihydroxylation product is a mixture of the *cis*- and *trans*-forms as shown in Scheme 13. This indicates that the second hydroxide attack proceeds both from the *cis*- and *trans*-positions. Under several conditions, epoxides are obtained, which are eventually hydrolyzed to *trans*-diols.

Alkyl transition metal complexes are generally known to react with electrophiles, such as protic acids and halogens, to generate organic compounds. The novel electrophilicity of the alkylplatinum(III) complex can arise from the strong electron-withdrawing ability of the high oxidation state of Pt^{III}. Nucleophilic attack of water is possible on the alkyl carbon atom bound to Pt^{IV},[28—31] but Pt^{IV} is not usually coordinated by olefin, except in the presence of a special ligand to stabilize the complex.[32,33] An electrophilic Alk—Pt^{II} complex is reported, but that is also an exceptional case and requires a strong electron-withdrawing group in the ligand.[11] A Me—Hg^{II} complex is also known to exhibit electrophilic properties[15] but Hg^{II} is not very reactive toward olefins. Considering these facts, Pt^{III} is a unique metal capable of both coordinating olefins and undergoing nucleophilic attack on the alkyl ligand.

The reaction of complex **7** with 1,3-dienes gives the 4-hydroxy-(*E*)-2-alkenyl-Pt^{III} complexes (Scheme 14). The structures of the complexes have been confirmed by

Scheme 13



X-ray crystallography.[34] All of the products undergo the second nucleophilic attack and the reaction finally produces (*E*)-alk-2-ene-1,4-diol exclusively.

Several dihydroxylation or epoxidation reactions of 1,3-conjugated dienes are known,[35,36] in which 1,2-diols (Scheme 15) or ene-epoxides are obtained as the major

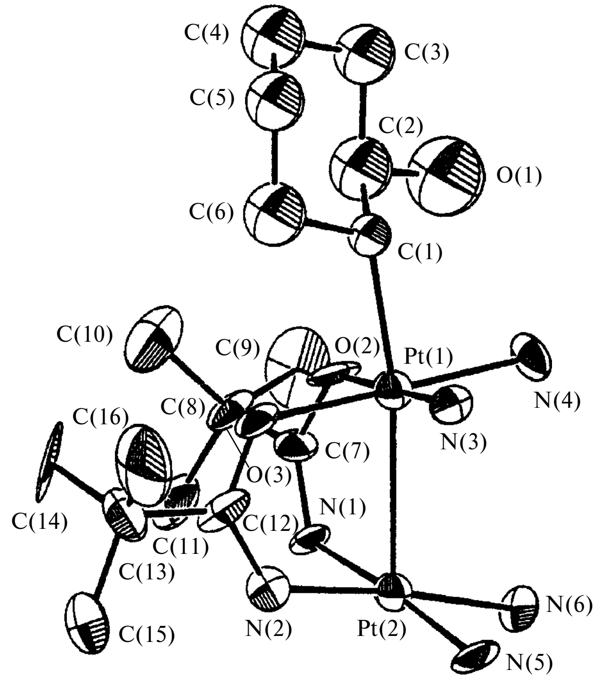
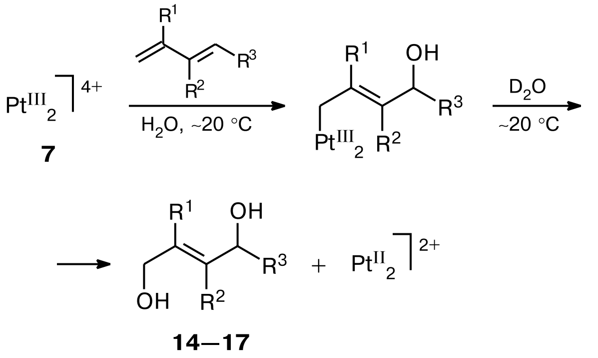


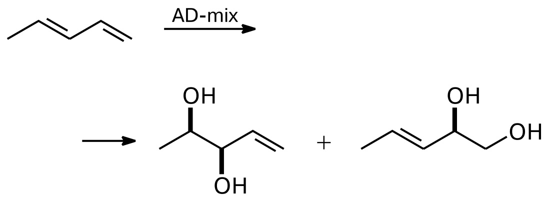
Fig. 6. Structure of complex **13** (thermal ellipsoids with 30% probability are presented).

Scheme 14



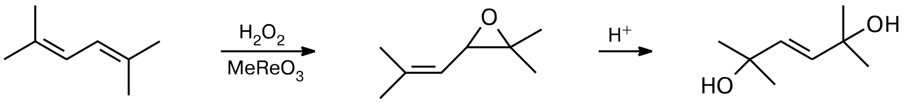
	R^1	R^2	R^3		R^1	R^2	R^3
14	H	H	Me	**16**	Me	H	Me
15	H	H	Et	**17**	H	Me	Me

Scheme 15

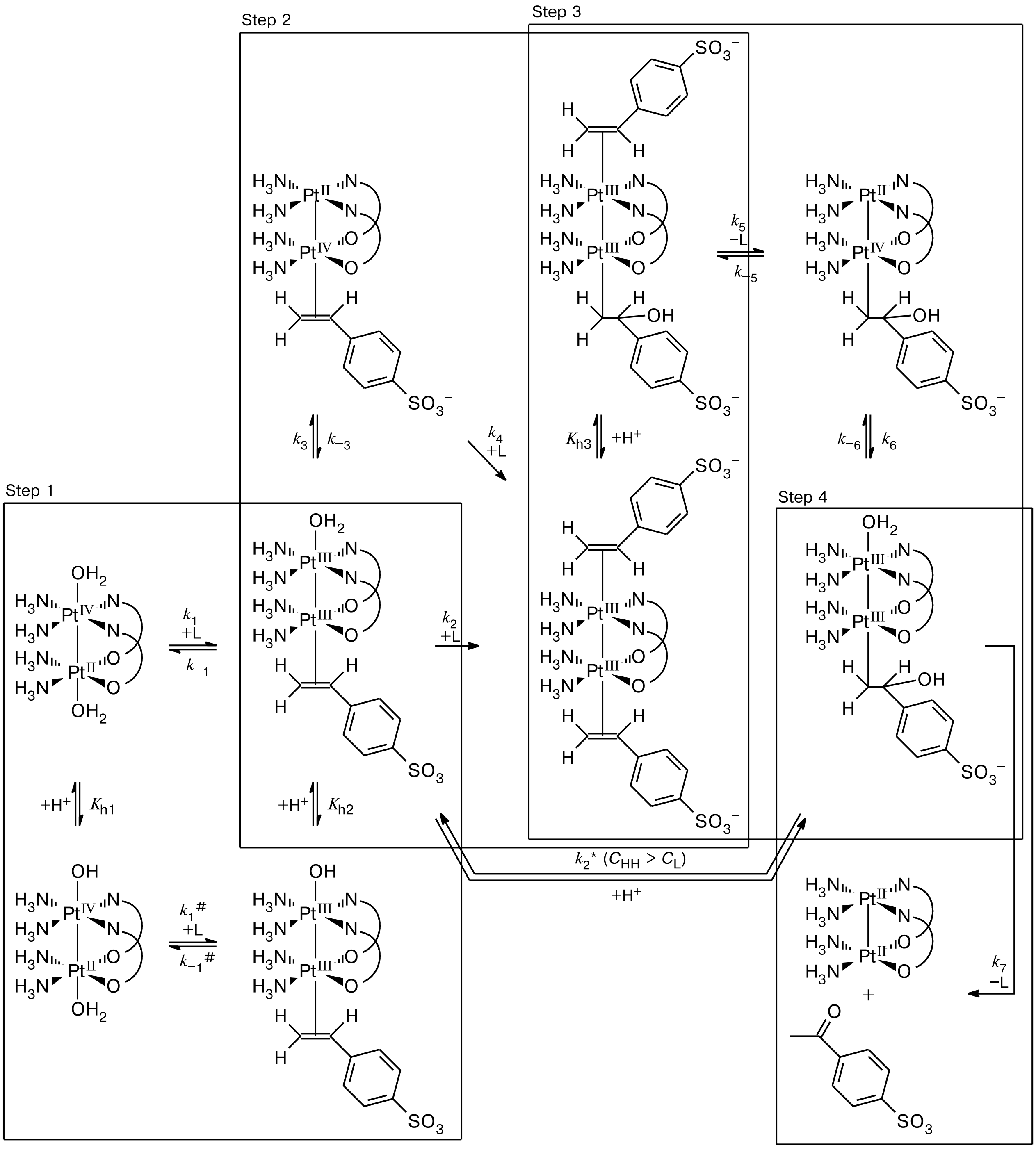


Ad-mix is asymmetrically dihydroxylating agent $K_2Os(OH)_4$ + + $(DHQD)_2PHAL$,
$(DHQD)_2PHAL$ is 1,4-bis(9-*O*-dihydroquinidinyl)phthalazine

Scheme 16



Scheme 17



products. Ene-1,4-diols are obtained only as minor products only in the reaction of the internal diene *via* ene-epoxides (Scheme 16). Terminal dienes did not give such ene-1,4-diols previously, and in this sense the reaction (see Scheme 14) is the first reaction to give stereoselectively (*E*)-ene-1,4-diols from wide variety of conjugated dienes.

Amphoteric nature of the Pt—Pt bond through electron delocalization

The above synthetic study and the olefin oxidation reactions show the nature of the Pt^{III} complexes as follows: (i) olefins coordinate to Pt^{III} at the axial position, in contrast to the π-coordination of olefins perpendicular to the square-planar coordination plane of Pt^{II} and the lack of olefin coordination to Pt^{IV}; (ii) Pt^{III} is strongly electron-withdrawing atom, and the coordinated olefins undergo nucleophilic attack; (iii) alkyl α-carbon on the Pt^{III} undergoes nucleophilic attack in an aqueous solution, whereas in aprotic solvents aldehyde (and possibly also ketone in other cases) is produced by reductive elimination.

In order to confirm the mechanism of the olefin reactions, kinetic study was carried out with stopped-flow UV spectroscopy.[14] From the kinetic study of the reaction of **7** with *p*-styrenesulfonic acid in an aqueous solution, the mechanism shown in Scheme 17 was driven in which the approximate and tentative platinum oxidation states are assigned based on the axial coordination mode. The mechanism shows that the electron distribution along the Pt—Pt bond is surprisingly flexible and the electrons move from one Pt atom to the other very quickly depending on the axial ligand.

The $Pt^{III}—Pt^{III}$ bond in the alkyl complexes exhibits unique character that the Pt atoms act both as Pt^{II} and Pt^{IV} or the intermediate Pt^{III} though electron delocalization along the Pt—Pt axis: (i) coordination of olefin is a Pt^{II} characteristic, since no olefin—Pt^{IV} complexes is known except one and (ii) nucleophilic attack on the coordinated alkyl α-carbon atom occurs, which is characteristic of Pt^{IV}, whereas similar nucleophilic attack does not occur on α-carbon atoms of alkyl—Pt^{II} complexes.[28,29,37]

The electron localization ($Pt^{IV}—Pt^{II}$) and delocalization ($Pt^{III}—Pt^{III}$) through the Pt—Pt bond seem to depend on the nature of the axial alkyl ligand and polarity of the solvent. With this unique electron buffer function of the Pt—Pt bond, the present alkyl complexes are stabilized and exhibit various reactivities. The relative stability of the alkyl (σ) and olefin (π) complexes of Pt^{III} and Pt^{II} can be easily seen by comparison of the crystal structures of the π-complex of Pt^{II} with vinyl alcohol[24—26] and the 2-oxyethyl σ-alkyl complex of Pt^{III} (compound **11**). The bond distances and angles suggest that although compound **11** is a σ-complex, the ligand is actually intermediate between the σ-alkyl and π-olefin complexes. This should be compared with the structure of the π-complex of Pt^{II} with vinyl alcohol and suggests that, since Pt^{III} is more strongly electron-withdrawing atom than Pt^{II}, the coordinated vinyl alcohol on Pt^{III} is more acidic, and thus the alkyl complex is more favored than that of Pt^{II}.

The strong electron-withdrawing nature of Pt^{III} leads to the unique reactions of Pt^{III} dinuclear complexes. The structural features of Pt^{III} dinuclear complexes, *i.e.*, axial ligand addition and release corresponding to the Pt^{III} and Pt^{II} oxidation state, make the axial position of the dinuclear complex an attractive reaction site. This attractive and unique property is further reinforced by the electron delocalization flexibility of the $Pt^{III}—Pt^{III}$ bond *trans* to the axial reacting ligand, and gives the platinum atoms both Pt^{II} and Pt^{IV} characters. The bond is approximately $L—Pt^{II}—Pt^{IV}$ or $L—Pt^{III}—Pt^{III}$ when the olefin L is π-coordinated, whereas the bond is close to a σ-bond as in $R—Pt^{IV}—Pt^{II}$ when the olefin complex undergoes nucleophilic attack and becomes an alkyl complex. This class of the Pt^{III} complexes, in this way, provides the unique and unprecedented reaction centers.

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