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Organometallic chemistry of platinum-blue derived platinum^{III} dinuclear complexes

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Abstract

The pivalamidate-bridged Pt^{III} dinuclear complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(H_2O)_2]^{4+}$ (**3**) reacts with ketones in water to give the ketonyl complexes $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4L]^{3+}$, where L is ketonyl and in most cases the α-C–H of the ketone is deprotonated. The α-C–H activation of the ketone proceeds both by homolytic cleavage and electrophilic displacement of proton by Pt^{III}. Complex **3** reacts also with olefins in water to give β-hydroxyalkyl Pt^{III} dinuclear complexes. In acidic water, these complexes release ketones or epoxides and the Pt^{III} dinuclear complexes are reduced to the corresponding Pt^{II} dinuclear complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4]^{2+}$. When the solution is saturated with O_2, the olefin oxidation proceeds catalytically. The reaction mechanism is basically similar to the Wacker process. In neutral to basic solution the α-carbon atoms of the β-hydroxyalkyl Pt^{III} complexes undergo nucleophilic attack by water, and α,β-dihydroxyalkanes are released. Complex **3** reacts also with alkynes in water to give the ketonylplatinum^{III} dinuclear complexes. All of the above reactions show that the Pt^{III} dinuclear complex has both Pt^{II} and Pt^{IV} characters; coordination of olefins is a Pt^{II} character, whereas nucleophilic attack on the coordinated α-carbon atom is a Pt^{IV} character. The electron delocalization and flexibility along the Pt–Pt bond make these unique characters of the Pt^{III} complex possible. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Pt^{III}-dinuclear complexes; Ketone

1. Introduction

Platinum^{III} is an unusual oxidation state, and can be isolated only in certain structural types using special ligands for stabilization. Historically the first platinum^{III} compound was reported as ‘Platin Blau’, obtained when German researchers allowed *cis*-Pt^{II}Cl$_2$(CH$_3$CN)$_2$ with Ag_2SO_4 to react in water to form a dark blue uncharacterized precipitate [1]. The dark blue color of this product was later found to indicate the mixed valent nature of the compound, after the compound had remained uncharacterized for many years. In the 1970s, when the interaction of the famous anti-cancer drug *cis*-Pt^{II}Cl$_2$(NH$_3$)$_2$ with DNA components, pyrimidine bases, was intensively studied, similar dark blue compounds were again observed. By using model amidate ligands, these products were first characterized as Pt^{II,III} mixed valent compounds of the general formula $[Pt_4(NH_3)_8L_4]^{5+}$ (Fig. 1) (L is deprotonated

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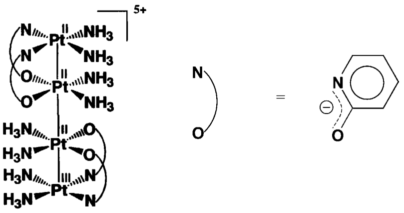


Fig. 1. The structure of α-pyridonate-bridged platinum blue.

amidate ligands) [2]. The blue compound was found to consist of $3 \times Pt^{II}$ and $1 \times Pt^{III}$, 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 $[Pt_2(NH_3)_4L_2L'_2]^{2+}$ (L′ is uni-negative axial ligands such as halide, nitrate or nitrite) and Pt^{II} dimers $[Pt_2(NH_3)_4L_2]^{2+}$, respectively (Fig. 2) [3–9].

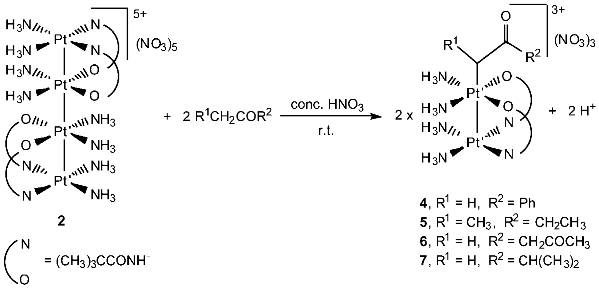
In addition to the above amidate-bridged dinuclear Pt^{III} complexes, sulfate– [10,11], phosphate– [10,11], carboxylate– [12], or diphosphito– [13,14] Pt^{III} dinuclear complexes, $[Pt_2(SO_4)_4XY]^{n-}$ (X and Y are axial ligands), $[Pt_2(HPO_4)_4XY]^{n-}$, $[\{(H_2O)Pt(\mu\text{-}CH_3CO_2)_2\}_2]A_2$ ($A = ClO_4^-$, $CF_3SO_3^-$), and $[Pt_2(P_2O_5H_2)_4CH_3I]^{2-}$, and the Pt^{III} dinuclear complexes even without a bridging ligand, $[Pt_2Cl_6\{(HNC(OH)C(CH_3)_3)_4\}$ [15] and $[Pt_2(CN)_{10}]^{4-}$ [16], are known. All of these complexes have a Pt–Pt metal–metal bond and each Pt^{III} atom has an octahedral environment. This structural motif appears to be common to all the dinuclear platinum compounds and is essential to stabilize the Pt^{III} oxidation state. A mononuclear Pt^{III} complex is known only in one case, namely $(NBu_4)[Pt(C_6Cl_5)_4]$ [17].

The amidate-bridged dinuclear Pt^{III} complexes in Fig. 2 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 towards nucleophilic attack or electrophilic attack.

In this article, organometallic chemistry of amidate-bridged dinuclear Pt^{III} complexes at the axial positions is reviewed. All of this organometallic chemistry has been studied in the author's group. In this work an unexpectedly high affinity of Pt^{III} towards various organic molecules has been observed.

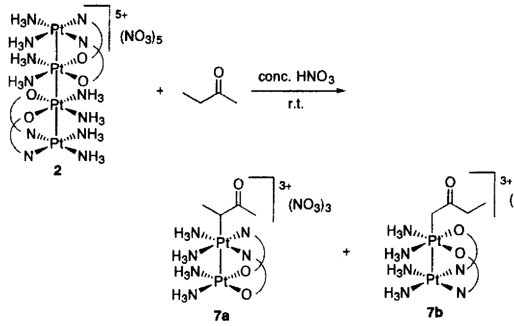
2. Ketonylplatinum^{III} dinuclear complexes

The first ketonyl–Pt^{III} dinuclear complex with a pivalamidate bridging ligand, $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_3)](NO_3)_3$ (**1**) [18,19] was prepared by the reaction of a $Pt^{II,III}$ 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 (Eq. (1)). The acetonyl carbon is bound axially to one of the Pt^{III} atoms in **1**, while the other Pt^{III} atom has the nitrate as a weakly coordinated axial ligand (Fig. 3). In contrast to most alkyl–transition metal complexes, **1** was prepared in acidic aqueous solution.



(1)

Butanone having two different α-C–H bonds gave a mixture of two ketonyl–Pt^{III} complexes, namely $[Pt_2(C_5H_{10}NO)_2(NH_3)_4(CH(CH_3)COCH_3)](NO_3)_3$ (**7a**) and $[Pt_2(C_5H_{10}NO)_2(NH_3)_4(CH_2COCH_2CH_3)](NO_3)_3$ (**7b**), in a molar ratio of 1.7:1 (Eq. (2)). However, the reaction with 3-methyl-2-butanone afforded only one complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCHMe_2)](NO_3)_3$ (**8**) exclusively as a result of α-methyl C–H bond activation (Eq. (1)).



(2)

The carbon atom bound directly to the Pt^{III} atom was found to undergo nucleophilic attack in water. For instance, **1** reacts with water or NaOH and NaBr to release α-hydroxyacetone and α-bromoacetone, and the Pt^{III} dinuclear complex **1** is reduced to the corresponding Pt^{II} dinuclear complex. Similarly, all of the ketonyl Pt^{III} complexes in Eq. (1) react with water or NaOH and $HNEt_2$ to release the α-hydroxy-substituted and α-aminated ketones (Eq. (3)).

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 [20]. A methyl–Hg^{II} complex is also known to exhibit electrophilic properties [21]. Except for these few rare cases,

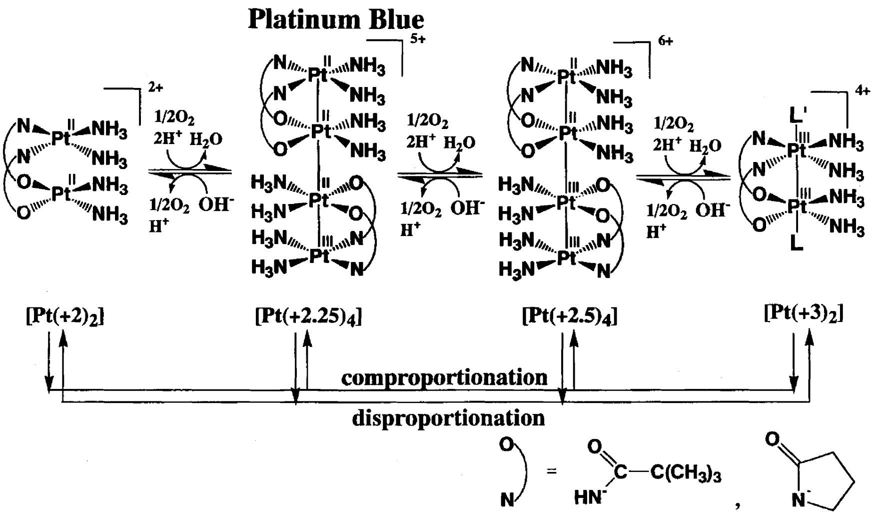
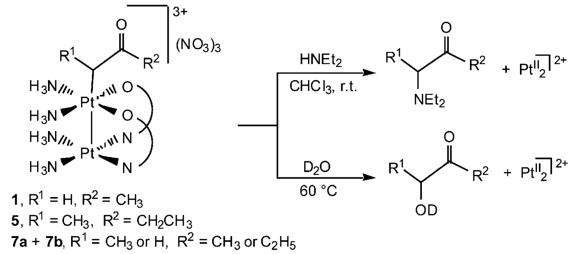


Fig. 2. The redox behavior of the platinum blue complexes.



(3)

electrophilic alkyl–metal complexes are rare, and in this sense, Pt(III) complex are valuable.

Formation of a number of ketonyl transition metal complexes is reported to proceed via (i) the reaction of ketone with a hydroxyl complex or a complex having a basic ligand, (ii) the reaction of ketone with a low-valent transition metal complex in the presence of a base, and (iii) oxidative addition of a chloroketone or an α-C–H bond of ketone to a low-valent transition metal complex [22–27]. 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} dimeric complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(H_2O)_2](NO_3)_4$ (**3**) has been shown to be the active species. In fact, complex **1** can be prepared also from previously isolated complex **3** [28,29], and therefore, oxidative addition of acetone to the mixed valent lower oxidation state complex **2** is excluded as the possible formation mechanism for **1**. For the C–H activation of acetone the three routes shown in Scheme 1 can be conceived as the reaction path.

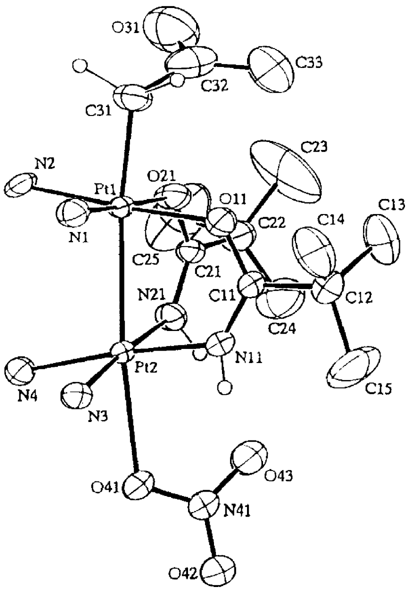
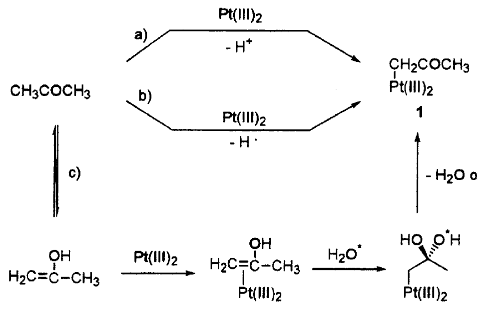


Fig. 3. The X-ray structure of $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_3)(NO_3)]^{2+}$.

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 elim-



Scheme 1.

inate one molecule of H_2O. 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.

To identify the real reaction pathway, the acetonylplatinum^{III} complex **1** was prepared in the presence of $H_2^{18}O$ by using either HNO_3 or $Na_2S_2O_8$ as the oxidant. Treatment of this platinum^{III} complex **1** with $HNEt_2$ gave aminoacetone, which was identified by GC-MS to contain exclusively the ^{16}O isotope. This result excludes the possibility of C–H activation of acetone via the enol form as in route c of Scheme 1, since route c will give aminoacetone with both ^{16}O and ^{18}O isotopes approximately in a 1-to-1 distribution. It may also seem possible that, slightly different from route c, **1** is produced by deprotonation of the coordinated enol π-complex. In this case, no ^{18}O incorporation would be expected. However, in the reaction with ethylene, both the hydroxyethylene π-complex and its deprotonated β-ketonyl complex were observed in equilibrium in the ^1H-NMR spectrum of the aqueous solution (see next section). In the present experiment, however, no such π-complex of the coordinated enol was observed. As later discussed in the reaction with ethylene, the π-coordinated monohydroxylethylene complex receives the second hydroxylation (Eq. (8)), and from this fact, it is improbable that ^{18}O is not incorporated, if the enol form participates in the reaction. Therefore, involvement of the enol form in the reaction path was disregarded.

Since route c has been excluded, the routes a and b remain to be considered. Of particular interest and importance is the observation of two complexes **7a** and **7b** obtained as a mixture in a molar ratio of 1.7:1 in the reaction of the Pt^{III} complex **3** with butanone in the presence of concentrated nitric acid at room temperature (r.t.) under room light. This may indicate competition between the two processes of radical and electrophilic displacement in the reaction. It was found that the relative molar ratio of **7a** to **7b** depends on the reaction conditions. Change of the light source from room light to a mercury lamp increases the **7a/7b** ratio, whereas this ratio decreases when the reaction is carried out in the dark, and decreases markedly when a radical trapping agent, 2,4,6-tri-*tert*-butylphenol, is added. These results strongly support that the complex **7a** is formed via a radical mechanism, in which the $CH_3COCH\cdot(CH_3)$ radical is the intermediate. The fact that the presence of a radical trapping agent does not suppress the formation of complex **7b** strongly suggests that **7b** is formed by a different mechanism. The electrophilic displacement as shown in route a (Scheme 1) is reasonable for the formation of complex **7b**. This is the first clear observation of the competitive mechanisms occurring simultaneously, i.e. a radical pathway and an electrophilic displacement in a transition metal-promoted C–H bond activation, although both mechanisms have been proposed separately in many reaction systems. The yields decrease slightly when the reactions are carried out under light, which can be a consequence of radical side reactions.

3. 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 (Fig. 2). 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 $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 2H_2O$ (**8**) or pivalamidate-bridged platinum blue compound $[Pt_4(NH_3)_8(C_5H_{10}NO)_4](NO_3)_5$ (**9**) as the catalyst in an acidic H_2O–CH_2ClCH_2Cl biphasic solution [28,29]. In a typical experiment, 10 μmol 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 2-ketones, whereas cyclic olefins (cyclohexene and norbornene) are selectively oxidized to epoxides. The linear internal olefin 2-octene is oxidized to both 2- and 3-octanones.

Although the oxygen atom in the products had 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 did not exist in the products. The true catalyst was also confirmed to be the Pt^{III} dinuclear complexes, $[Pt_2(NH_3)_4(C_4H_6NO)_2(H_2O)_2]^{4+}$ (**10**) and $[Pt_2(NH_3)_4(C_5H_{10}NO)_2(H_2O)_2]^{4+}$ (**11**) [28]. From these facts, it was conceived that the reaction mechanism is similar to the Wacker reaction as shown in Fig. 4. 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 oxidizing 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 platinum blue compounds

Substrate	Product	Turnover number [a]	
		Catalyst 8	Catalyst 9
1-Hexene	2-Hexanone	11.9	3.8
	1,2-Epoxyhexane	8.6	8.8
1-Heptene	2-Heptanone [b]	13.3	4.5
1-Octene	2-Octanone [b]	15.8	12.4
1-Decene	2-Decanone	10.9	4.1
2-Octene	2-Octanone	1.7	1.6
	3-Octanone	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
	Norbornanone [d]	2.3	0.6
2-Methyl-2-butene	3-methyl-2-butanone		
Ethyl vinyl ether	Acetaldehyde		
	Ethyl alcohol		
1-Chloro-1-propene			No reaction
1-Bromo-1-propene			No reaction
α-Methylstyrene			No reaction
β-Methylstyrene			No reaction
Allylbenzene			No reaction

[a] Turnover number = [product]/[complex].
[b] Minor product (less than 1%) 1,2-epoxide.
[c] Minor product (less than 1%) cyclopentanecarboxyaldehyde.
[d] Minor product (less than 1%) norborneol.

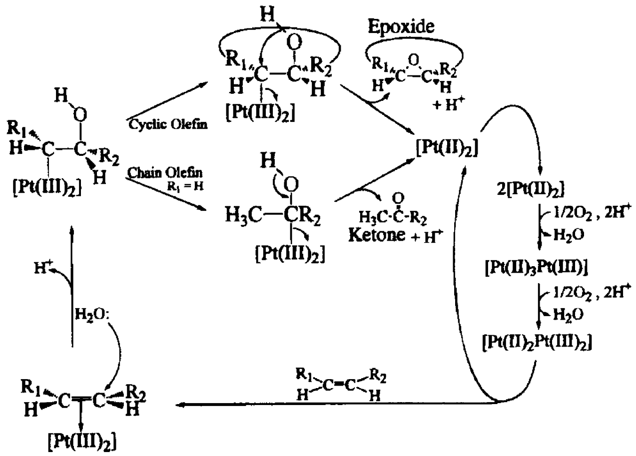
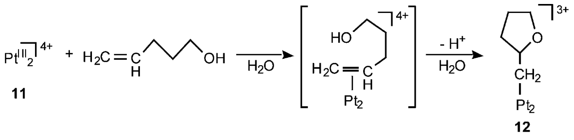


Fig. 4. Proposed reaction mechanism for olefin ketonation and epoxidation catalyzed by platinum blue.

4. Alkylplatinum$^{\mathrm{III}}$ dinuclear complexes prepared from alkenes

The proposed reaction mechanism for the olefin oxidation (Fig. 4) suggests that olefins π-coordinate axially to Pt$^{\mathrm{III}}$. If so, it is very scientifically meaningful, since Pt$^{\mathrm{II}}$ coordinates olefins in the equatorial plane, whereas Pt$^{\mathrm{IV}}$ does not coordinate olefins, except in a very few special complexes. Isolation of Pt$^{\mathrm{III}}$–olefin complexes would be the first proof of the olefin coordination in the Pt$^{\mathrm{III}}$ chemistry. If the mechanism proposed in Fig. 4 is correct, it also shows that a 1,2-shift occurs on Pt$^{\mathrm{III}}$ similar to Pt$^{\mathrm{II}}$, and the carbon atom on the Pt$^{\mathrm{III}}$ undergoes nucleophilic attack. If these are proved, they would construct the fundamental chemistry of Pt$^{\mathrm{III}}$. Attempts to isolate the Pt$^{\mathrm{III}}$ π-complex were unfortunately not successful either in aqueous or organic solvents. However, alkyl Pt$^{\mathrm{III}}$ complexes were unexpectedly obtained. Their structures and solution behavior indicate the typical nature of Pt$^{\mathrm{III}}$ as explained below.

Isolation of the reaction products with simple mono-olefins was at first not easy, and the first product obtained was with hydroxy-substituted olefins as shown in eqs 4 and 5 [29]. The structures of the products $[\mathrm{Pt}_2^{\mathrm{III}}(\mathrm{NH}_3)_4((\mathrm{CH}_3)_3\mathrm{CCONH})_2(\mathrm{CH}_2\mathrm{CH}(\mathrm{CH}_2)\mathrm{O})](\mathrm{NO}_3)_3 \cdot \mathrm{H}_2\mathrm{O}$ (**12**) and $[\mathrm{Pt}_2^{\mathrm{III}}(\mathrm{NH}_3)_4((\mathrm{CH}_3)_3\mathrm{CCONH})_2(\mathrm{CH}_2\mathrm{CHO})](\mathrm{NO}_3)_3 \cdot \mathrm{H}_2\mathrm{O}$ (**13**) are shown in Figs. 5 and 6.



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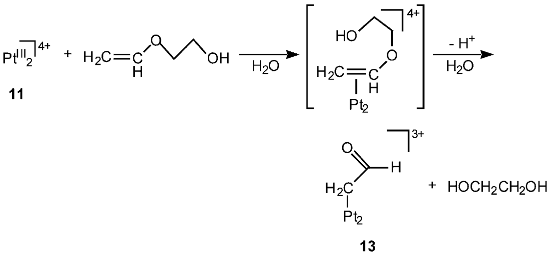
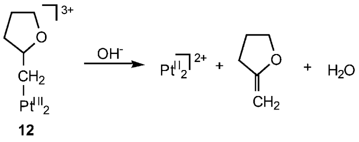


(5)

In most of the alkyl Pt$^{\mathrm{III}}$ complexes, the axial position *trans* to the alkyl group via the Pt$^{\mathrm{III}}$–Pt$^{\mathrm{III}}$ bond is vacant owing to the large *trans* effect of the alkyl group. In the acetonyl complex in Fig. 3, the *trans* Pt–O(nitrate) distance is unusually long (2.667(7) Å). The bond distances of the alkyl group of **13** are shown in Fig. 7, which shows that the actual electronic structure is intermediate between a σ-ketonyl complex and a π-olefin complex.

Complex **12** is stable in acidic to weakly basic aqueous solution. However, upon addition of 0.1 M NaOH, nucleophilic attack occurs at the β-carbon as shown in Eq. (6). The reaction may also be considered to proceed via initial α-hydroxylation, which eventually leads to dehydration to give the product.



(6)

Complex **13** is unstable at r.t. even as a solid, and is easily hydrolyzed in neutral water to produce glycol

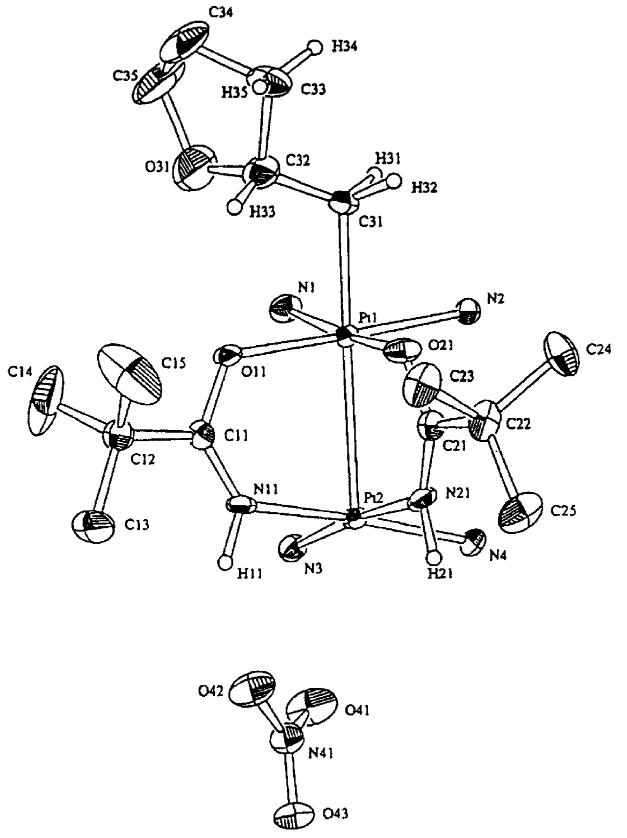


Fig. 5. ORTEP drawing of $[Pt_2(NH_3)_4((OH_3)_3CCONH)_2(CH_2CH(CH_2)_3O)](NO_3)_3H_2O$ (**12**).

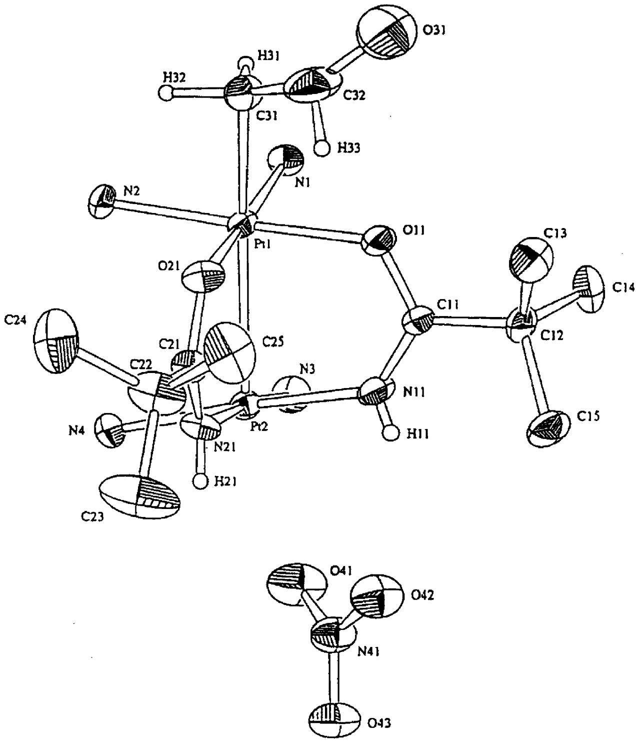
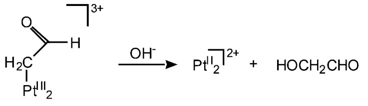


Fig. 6. ORTEP drawing of $[Pt_2(NH_3)_4((OH_3)_3CCONH)_2(CH_2CHO)](NO_3)_3H_2O$ (**13**).

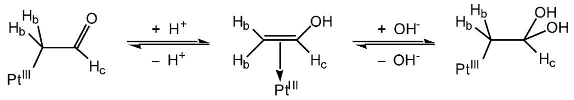
aldehyde (Eq. (7)). In 0.1 M $HClO_4$ **13** produces glycol aldehyde and acetic acid in a ca. 9:1 ratio.



13

(7)

The ^1H-NMR spectrum of **13** in D_2O is shown in Fig. 8. Different from what is expected for the crystal structure of **13**, 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–base equilibrium between the π-vinyl alcohol and β-oxoethyl structures as shown in Fig. 8. The ^1H chemical shifts of compound **13** are listed in Table 2. The assignment of the peaks has been 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 [30–32], 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 spectral pattern of the π-complex of **13** 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^{III} in acetone [30,31,33]. The reason for the A_2X pattern in **13** is probably as follows. The π-complex of **13** is in equilibrium with the dihydroxyethyl form, and exchange of the two forms is rapid, as shown below.



(8)

5. Dihydroxylation of mono and dienes with the Pt^{III} dinuclear complex

The previous section describes nucleophilic attack of the α-carbon atom on the dinuclear Pt^{III} complex **2**, indicating that consecutive dinucleophile addition can be achieved onto the alkenes as shown in Scheme 2. Such consecutive double nucleophilic attack had not been realized on any metal.

The reaction of the pivalamidate-bridged Pt^{III} dinuclear complex **2** with cyclic mono olefins gave 1,2-disubstituted cyclic alkanes as expected [37] (Scheme 3). Interestingly, the β-hydroxy cyclohexyl complex was isolated as an intermediate, and the crystal structure clearly shows that the hydroxylation occurs by *trans*

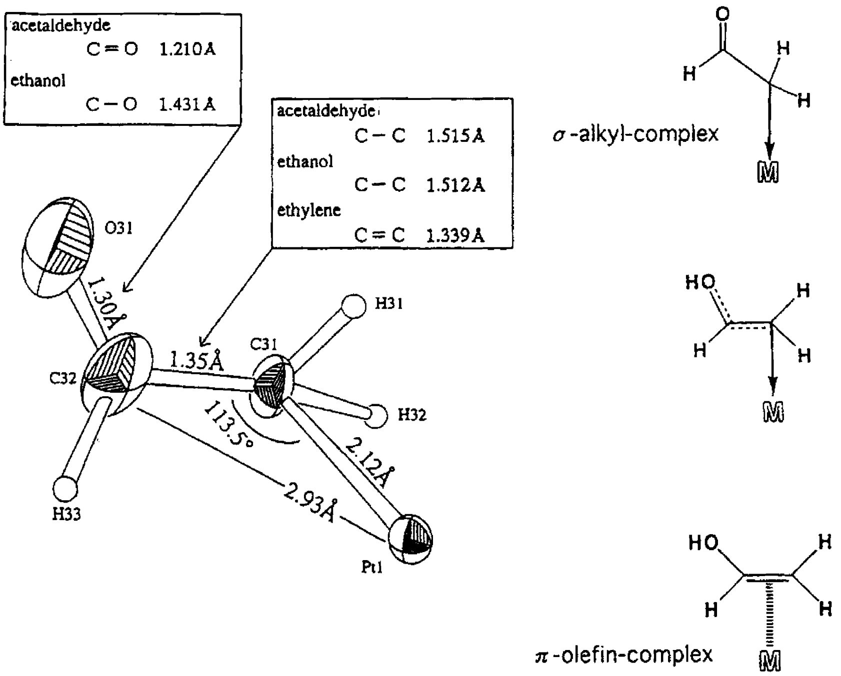


Fig. 7. Bond distances and angles of the β-oxyethyl group in **13**.

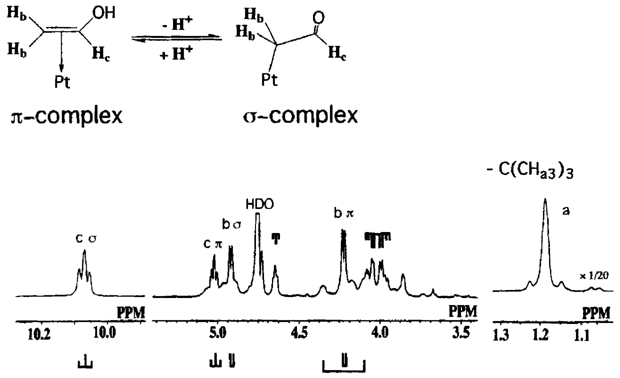


Fig. 8. ^{1}H-NMR spectrum of **13** in D_2O. The small peaks at around 4.0 and 4.6 ppm are not known. They are probably decomposition products.

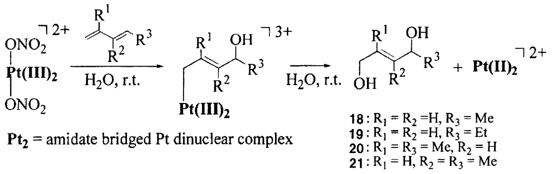
Table 2
^{1}H-NMR chemical shifts and coupling constants for **13** in D_2O

	π-complex	σ-complex
$\delta(H_a)$ (ppm)	1.18	1.17
$\delta(H_a)$ (ppm)	4.19	4.88
$\delta(H_a)$ (ppm)	5.01	10.05
$^3J(H_b-H_c)$ (Hz)	4.3	4.3
$^2J(Pt-H_b)$ (Hz)	69	

addition (Fig. 9). The dihydroxylation product is a mixture of *cis* and *trans* forms as shown in Scheme 3.

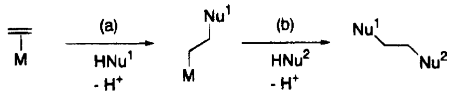
Alkyl–transition-metal complexes are generally known to react with electrophiles, such as protic acids and halogens, to generate organic compounds. The novel electrophilicity of the alkylplatinum^{III} complex can arise from the strong electron-withdrawing ability of the unusually high oxidation state of the Pt^{III} atom. Nucleophilic attack of water is possible on the alkyl carbon atom bound to a Pt^{IV} [35,36,38,39], but Pt^{IV} is not usually coordinated by olefin, except in the presence of a special ligand to stabilize the complex [40,41]. An electrophilic alkyl–Pt^{II} complex is reported, but that is also an exceptional case and requires a strong electron-withdrawing group in the ligand [20]. A methyl–Hg^{II} complex is also known to exhibit electrophilic properties [21], 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 **2** with 1,3-dienes gives 4-hydroxy-(*E*)-2-alkenyl–Pt^{III} complexes as shown in Eq. (9). The structures of the complexes have been confirmed by X-ray crystallography [42]. All of the products undergo a second nucleophilic attack and the reaction finally releases (*E*)-2-alkene-1, 4-diol exclusively.



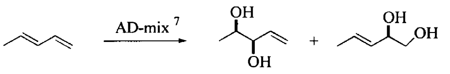
(9)

Several dihydroxylation or epoxidation reactions of 1,3-conjugated dienes are known [43,44], in which 1,2-diols (Eq. (10)) or ene-epoxides are obtained as the

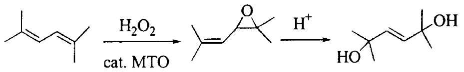


Scheme 2.

major products. Ene-1,4-diols are obtained only as minor products in the reactions of internal dienes via ene-epoxides (Eq. (11)). Terminal dienes did not give such ene-1,4-diols previously, and in this sense the reaction in Eq. (9) is noteworthy.



(10)



(11)

6. Amphoteric nature of the Pt–Pt bond through electron delocalization

The above synthetic study and the olefin oxidation reactions show the nature of 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, and the coordinated olefins undergo nucleophilic attack. (iii) The alkyl α-carbon on the Pt^{III} undergoes nucleophilic attack in aqueous solution, whereas in aprotic solvents, aldehyde (and possibly also ketone in other cases) is produced by reductive elimination.

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 through electron delocalization along the Pt–Pt axis: (i) coordination of olefin is a Pt^{II} characteristic, since no olefin–Pt^{IV} complexes are known 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 [34–36].

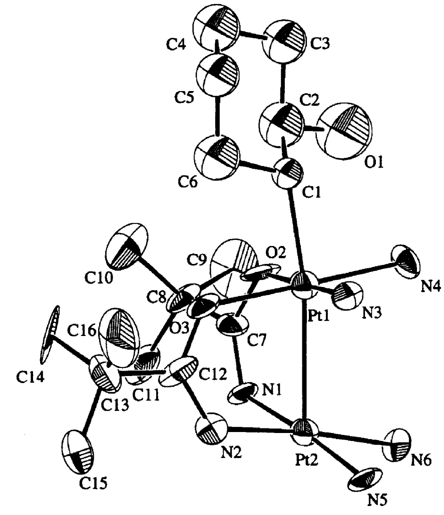
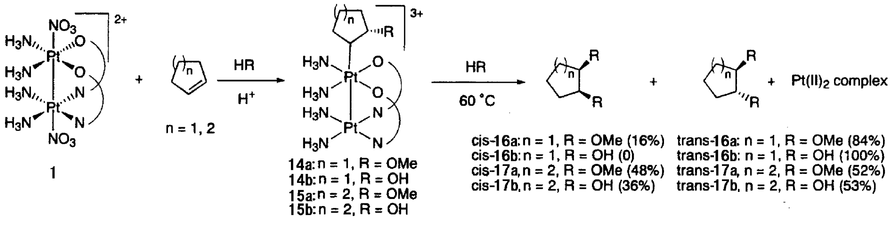


Fig. 9. ORTEP drawing of complex **15b**. Thermal ellipsoids are at the 30% probability level.

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) to olefin (π) complex on Pt^{III} and Pt^{II} can be easily seen by comparison of the crystal structures of the vinyl alcohol π-complex of Pt^{II} [30–32] and the 2-oxyethyl σ-alkyl complex of Pt^{III} (compound **13**). The bond distances and angles suggest that although **13** 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 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}.

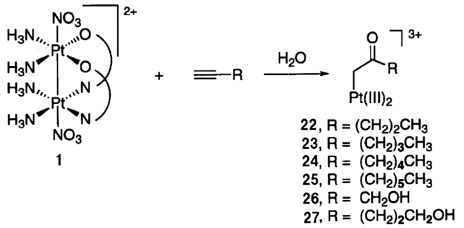
7. Ketonylplatinum^{III} dinuclear complexes prepared from alkynes

Addition of terminal alkynes CH≡CR to an aqueous solution of the platinum^{III} dinuclear complex **3** at r.t. was found to give the corresponding ketonyl–Pt^{III} dinuclear complexes as shown in Eq. (12). The internal alkyne, 2-butyne, also forms the ketonyl complex as in

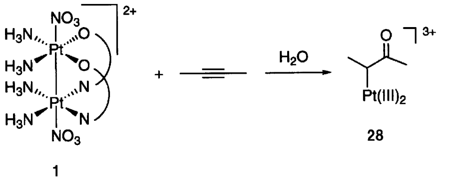


Scheme 3.

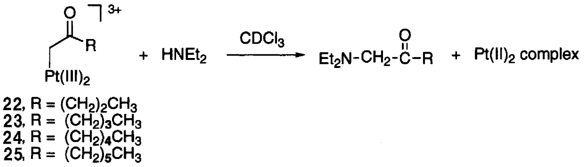
Eq. (13). These ketonyl complexes undergo nucleophilic attack, and aminoketones are released as in Eq. (14) [45]. These reactions represent unique alkyne conversions to aminoketones, and are a result of the strong electron withdrawing property of Pt^{III}. More variations of the reactions are being studied.



(12)



(13)



(14)

8. Conclusion

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 states 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} 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 unique reaction centers.

References

[1] K.A. Hofmann, G. Bugge, Berichte 41 (1908) 312.
[2] J.K. Barton, H.N. Rabinowitz, D.J. Szalda, S.J. Lippard, J. Am. Chem. Soc. 99 (1977) 2827.
[3] K. Matsumoto, K. Fuwa, Chem. Lett. (1984) 569.
[4] K. Matsumoto, H. Takahashi, K. Fuwa, J. Am. Chem. Soc. 106 (1984) 2049.
[5] T. Abe, H. Moriyama, K. Matsumoto, Inorg. Chem. 30 (1991) 4198.
[6] K. Matsumoto, H. Miyamae, H. Moriyama, Inorg. Chem. 28 (1989) 2959.
[7] T.V. O'Halloran, M.M. Roberts, S.J. Lippard, J. Am. Chem. 106 (1984) 6427.
[8] L.S. Hollis, S.J. Lippard, J. Am. Chem. Soc. 103 (1981) 6761.
[9] L.S. Hollis, M.M. Roberts, S.T. Lippard, Inorg. Chem. B22 (1983) 3637.
[10] T.G. Appleton, J.R. Hall, D.W. Neale, Inorg. Chem. Acta 104 (1985) 19.
[11] T.G. Appleton, J.R. Hall, D.W. Neale, S.F. Ralph, Inorg. Chem. Acta 77 (1983) L149.
[12] C.H.L. Kennard, M. Matsumato, R. Stranger, Inorg. Chem. 34 (1995) 5646.
[13] C.M. Che, W.P. Schaefer, H.B. Gray, M.K. Dickson, P.B. Stein, D.M. Roundhill, J. Am. Chem. Soc. 104 (1982) 4253.
[14] C.M. Che, T.C.W. Mak, H.B. Gray, Inorg. Chem. 23 (1984) 4386.
[15] R. Cimi, F.P. Fanizzi, F.P. Intini, G. Natile, J. Am. Chem. Soc. 113 (1991) 7805.
[16] M. Maliarik, J. Glasev, I. T'oth, Inorg. Chem. 37 (1998) 5452.
[17] R. Uson, J. Fornies, L.R. Falvello, M. Tomas, J.M. Casas, A. Martin, F.A. Cotton, J. Am. Chem. Soc. 116 (1994) 7160.
[18] K. Matsumoto, J. Matsunami, K. Mizuno, H. Uemura, J. Am. Chem. Soc. 118 (1996) 8959.
[19] Y.S. Lin, H. Misawa, J. Yamada, K. Matsumoto, J. Am. Chem. Soc. 123 (2001) 569.
[20] B.L. Bennett, J. Birnbaum, D.M. Roddick, Polyhedron 14 (1995) 187.
[21] R.A. Periana, D.J. Taube, E.R. Evitt, D.G. Loffler, P.R. Wentrcek, G. Voss, T. Masuda, Science 259 (1993) 340.
[22] E.M. Prolopchuk, H.A. Jenkins, R.J. Puddephatt, Organometallics 18 (1999) 2861.
[23] D.D. Wick, K.I. Goldberg, J. Am. Chem. Soc. 119 (1997) 10235.
[24] M.W. Holtcamp, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 119 (1997) 848.
[25] S.S. Stahl, J.A. Labinger, J.E. Bercaw, Angew. Chem. Int. Ed. Engl. 37 (1998) 2180.
[26] G.S. Hill, R.J. Puddephatt, Organometallics 17 (1998) 1478.
[27] S.S. Stahl, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 5961.
[28] K. Matsumoto, K. Mizuno, T. Abe, T. Kinoshita, H. Shimura, Chem. Lett. (1994) 1325.
[29] K. Matsumoto, Y. Nagai, J. Matsumami, K. Mizuno, T. Abe, R. Somazawa, J. Kinoshita, H. Shimura, J. Am. Chem. Soc. 120 (1998) 2900.
[30] M. Tsutsui, M. Ori, I. Francis, J. Am. Chem. Soc. 94 (1972) 1414.
[31] Y. Wakatsuki, S. Nozakura, S. Murahashi, Bull. Chem. Soc. Jpn. 42 (1969) 273.
[32] F.A. Cotton, J.N. Francis, B.A. Frenz, M. Tsutsui, J. Am. Chem. Soc. 95 (1973) 2483.
[33] J. Hillis, I. Francis, M. Ori, M. Tsutsui, J. Am. Chem. Soc. 96 (1974) 4800.
[34] J.A. Labinger, A.M. Herring, D.K. Lyon, G.A. Luinstra, J.E. Bercaw, Organometallics 12 (1993) 895.
[35] G.A. Luinstra, L. Wang, S.S. Stahl, J.A. Labinger, J.E. Bercaw, Organomet. Chem. 504 (1995) 75.
[36] A. Sen, M. Lin, L.C. Kao, A.C. Hutson, J. Am. Chem. Soc. 114 (1992) 6385.
[37] Y.-S. Lin, S. Takeda, K. Matsumoto, Organometallics 18 (1999) 4897.

[38] A.C. Hutson, M. Lin, N. Basickes, A. Sen, J. Organomet. Chem. 504 (1995) 69.
[39] G.A. Luinstra, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 115 (1993) 3004.
[40] W.A. Howard, R.G. Bergman, Polyhedron 17 (1998) 803.
[41] E.J. Parsons, R.D. Larsen, P.W. Jennings, J. Am. Chem. Soc. 107 (1985) 1793.
[42] M. Ochiai, K. Matsumoto, Chem. Lett. (2002) 270.
[43] D. Xu, G.A. Crispino, K.B. Sharpless, J. Am. Chem. Soc. 114 (1992) 7570.
[44] H. Tan, J.H. Espenson, Inorg. Chem. 37 (1998) 467.
[45] Y.-S. Lin, J. Yamada, H. Misawa, K. Matsumoto, to be submitted.