Synthesis of Ketonylplatinum(III) Dinuclear Complexes: Observation of the Competitive Radical vs Electrophilic Displacement in Pt(III)-Promoted C−H Bond Activation of Ketones

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Abstract: New ketonylplatinum(III) dinuclear complexes $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COPh)](NO_3)_3$ (**4**), $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH(CH_3)COC_2H_5)](NO_3)_3$ (**5**), and $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_2COCH_3)](NO_3)_3$ (**6**) were prepared by treatment of platinum blue complex $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ (**2**) with acetophenone, 3-pentanone, and acetylacetone, respectively, in the presence of concentrated HNO_3. The structures of complexes **4** and **6** have been confirmed by X-ray diffraction analysis, which revealed that the C−H bonds of the methyl groups in acetophenone and acetylacetone have been cleaved and Pt(III)−C bonds are formed. Formation of diketonylplatinum(III) complex **6** provides a novel example of the C−H bond activation not at the central α-C−H but at the terminal methyl of acetylacetone. Reaction with butanone having unsymmetrical α-H atoms led to two types of ketonylplatinum(III) complexes $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH(CH_3)COCH_3)](NO_3)_3$ (**7a**) and $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_2CH_3)](NO_3)_3$ (**7b**) at a molar ratio of 1.7 to 1 corresponding to the C−H bond activation of methylene and methyl groups, respectively. Use of 3-methyl-2-butanone instead of butanone gave complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH(CH_3)_2)](NO_3)_3$ (**8**) as a sole product via C−H bond activation in the α-methyl group. The reactivity of the ketonylplatinum(III) dinuclear complexes toward nucleophiles, such as H_2O and $HNEt_2$, was examined. The α-hydroxyl- and α-amino-substituted ketones were generated in the reactions of $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_3)](NO_3)_3$ (**1**), **5**, and a mixture of **7a** and **7b** with water and amine, which indicates that the carbon atom in the ketonyl group bound to the Pt(III) atom can receive a nucleophilic attack. The high electrophilicity of the ketonylplatinum(III) complexes can be accounted for by the high electron-withdrawing ability of the platinum(III) atom. A competition between the radical and electrophilic displacement pathways was observed directly in the C−H bond activation reaction with butanone giving complexes **7a** and **7b**. Addition of a radical trapping agent suppressed the radical pathway and gave complex **7b** as the predominant product. On the contrary, **7a** was formed as the main product when the reaction solution was irradiated by mercury lamp light. These results together with other mechanistic studies demonstrate that complex **7a** was produced via a radical process, whereas complex **7b** is produced via electrophilic displacement of a proton by the Pt(III) atom. The competitive processes were further observed in the reactions of platinum blue complex **2** with a mixture of acetone and 3-pentanone in the presence of HNO_3. The relative molar ratio of acetonyl complex **1** to pentanoyl complex **5** was 3 to 1 under room light, whereas formation of complex **5** was almost suppressed when the reaction was carried out in the dark with the addition of a radical trapping agent.

Introduction

Platinum(III) has a very rare oxidation state and its organometallic chemistry has just begun to be explored.[1,2] The first pivalamidate-bridged ketonyl−Pt(III) dinuclear complex, $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_3)](NO_3)_3$ (**1**),[3] has been 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 HNO_3. 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. Different from most alkyl-transition metal complexes, **1** was prepared in acidic water and its carbon atom bound to the Pt(III) atom undergoes nucleophilic attack in water.[3] These rare properties and especially the novel facile C−H activation of acetone in the acidic condition have tempted us to explore a more general and detailed mechanism of the ketonyl C−H bond activation on a Pt(III) dinuclear complex.

As for the mechanism of C−H bond activation on transition metals, numerous studies have been reported.[4−8] However, it still seems controversial to draw any decisive conclusion. One

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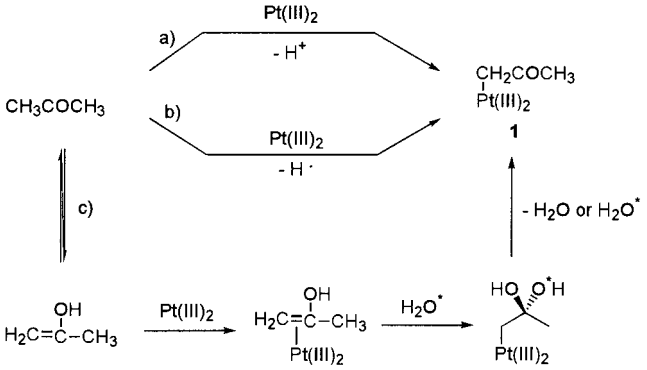
of the prevailing mechanisms is the oxidative addition of alkane protons, as first suggested by Shilov.[6,9,10] The C−H α-bond metathesis is another strongly suggested mechanism[6] especially by theoretical quantum chemists.[11]

There is also an increasing number of examples for oxidative C−H bond addition to a Pt(II) atom followed by formation of a Pt(IV) alkyl hydride intermediate in the Shilov reaction.[5a,12−14] Homolytic cleavage of a C−H bond is also reported for the alkane activation by metalloenzymes.[4−6] In the present study, the mechanism of the ketonyl C−H bond activation on the Pt(III) complexes is studied and is discussed in terms of the nature of the Pt(III)−C bond and the C−H bond activation. The comparison with Pt(II) organometallic chemistry would give a clear evaluation on how the novel Pt(III) can be a new entity in organometallic chemistry.

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 chloroketone or an α-C−H bond of ketones to a low-valent transition metal complex.[12−14] 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 on platinum blue complexes,[3] a platinum(III) dimeric complex $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(H_2O)_2](NO_3)_4$ (**3**) has been proved to be the real active species; In fact, complex **1** can be prepared also from the once isolated complex **3**, and the three routes shown in Scheme 1 can be conceived as the reaction route. Route a is an electrophilic displacement of H^+ in acetone by an electrophilic Pt(III) atom.[5,6] Homolytic cleavage of the C−H bond forming an acetonylplatinum(III) complex is another pathway (route b).[4−6] The last possibility is route c, in which the double bond of the enol form of acetone is coordinated to the Pt(III) atom, followed by nucleophilic attack of water and elimination of one molecule of H_2O. The nucleophilic attack on the double bond of alkenes promoted by a platinum(III) dimeric complex has been observed very recently.[18,19]

Scheme 1



Relatively few studies have been done on the properties of ketonyl transition metal complexes,[15a,20] although ketonyl transition metal complexes are important in organic synthesis such as alkylation reactions,[21] and for ketonyl−Pt(III) complexes, there is no report except the first one by our group.[3] Here we report a general synthetic method for the preparation of ketonylplatinum(III) dinuclear complexes and there reactivities. The mechanism of the C−H bond activation in ketones was also examined, which revealed the two competitive processes of electrophilic displacement and hemolytic cleavage. These properties are discussed in relation to the distinct properties of the Pt(III) atom and also the Pt(III)−Pt(III) metal−metal bonding.

Results and Discussion

Preparation of Ketonylplatinum(III) Dinuclear Complexes. The ketonylplatinum(III) dinuclear complexes, $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COPh)](NO_3)_3$ (**4**), $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH(CH_3)COCH_2CH_3)](NO_3)_3$ (**5**), and $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COCH_2COCH_3)](NO_3)_3$ (**6**), were obtained by treatment of the pivalamidate-bridged platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (**2**) with neat ketones, $PhCOCH_3$, $CH_3CH_2COCH_2CH_3$, and $CH_3COCH_2COCH_3$, respectively, in the presence of concentrated nitric acid at room

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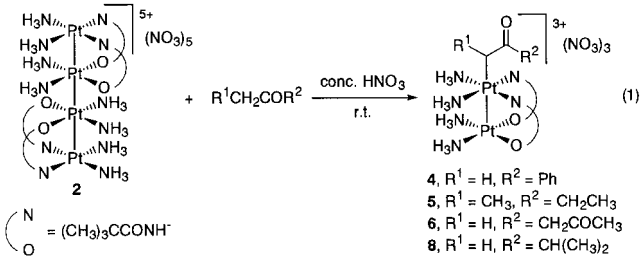
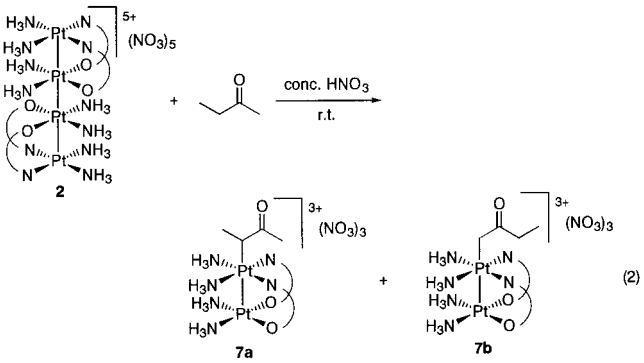
temperature (eq 1). It has already been confirmed that platinum



blue complexes are oxidized by HNO_3 or $Na_2S_2O_8$ totally to the corresponding Pt(III) dimmer complexes with H_2O, OH^-, NO_3^-, or NO^{2-} axial ligand.[22] Butanone having two different α-C−H bonds gave a mixture of two ketonyl−Pt(III) complexes, $[Pt_2(C_5H_{10}NO)_2(NH_3)_4(CH(CH_3)COCH_3)](NO_3)_3$ (**7a**) and $[Pt_2(C_5H_{10}NO)_2(NH_3)_4(CH_2COCH_2CH_3)](NO_3)_3$ (**7b**), at a molar ratio of 1.7 to 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).



All complexes obtained were identified by ^{1}H NMR spectra and elemental analysis as described in the Experimental Section. In complexes **4**, **6**, and **8**, the methylene protons bound to the Pt atom appear as singlets in the range of 5.5 to 4.8 ppm with the satellites of ca. 76 Hz separation. A quadruplet at 5.38 ppm with the satellites in the ^{1}H NMR spectrum of complex **5** can be attributed to the Pt-bonded methine proton. There the doublet at 0.06 ppm with satellites of 32 Hz separation in **5** can be assigned to the other methyl protons of the CH_3CHPt moiety, and is high-field shifted compared to the other methyl protons (0.88 ppm) of the 3-pentanonyl group. The existence of the satellites to the proton signal indicates the coupling to the ^{195}Pt nucleus, and shows that the proton is bound to the α-carbon atom.[23] In the ^{1}H NMR spectrum of the mixture of **7a** and **7b**, a singlet at 4.86 ppm with the satellite of 76 Hz can be assigned to the methylene protons bound to the Pt atom of complex **7b**, while the quadruplet at 5.39 ppm with 78 Hz satellites belongs to the methine proton of complex **7a**, and the methyl group bound to the methine again appears at higher field (0.11 ppm). The structures of complexes **4** and **6** were further confirmed crystallographically.

Structure Analysis of Complex 4·PhCOCH$_3$ and 6. Yellow crystals of **4**·$PhCOCH_3$ and **6** were obtained by addition of acetophenone and acetylacetone, respectively, to an aqueous solution of Pt(III) dimeric complex **3** prepared in situ by the oxidation of platinum blue complex **2** with $Na_2S_2O_8$ in the presence of concentrated HNO_3. Both structures were identified by X-ray diffraction analysis. The ORTEP drawings of the cations of complexes **4** and **6** are given in Figures 1 and 2, respectively. Formation of complex **6** with the activation of the terminal methyl group is in contrast to the well-known activation of the central methylene group in *β*-diketones.[24] Only one other example is known for such bond formation at the less acidic α-carbon atoms of *β*-diketones, i.e., the external α-carbon atom bound to a mercury atom, where, however, the internal carbon atom is bound to a bulky substituent.[25] The bond length of Pt−C is 2.15 (2) Å in **4** and 2.114 (8) Å in **6**. The former is comparable to that in the acetonyl−Pt(III) dinuclear complex (2.14 Å)[3] and to the corresponding bond length in the acetophenonyl−Pt(II) complex (2.175 Å).[15g] The short bond lengths of C(2)−C(3) (1.39(1) Å) and C(3)−C(4) (1.44(2) Å) and the long ones of O(1)−C(2) (1.30(1) Å) and O(2)−C(4) (1.26(2) Å) in **6** show conjugation of the diketonyl moiety. The angle of C(2)−C(3)−C(4) (119(1)°) implies sp^2 hybridization of the C(3) atom. The

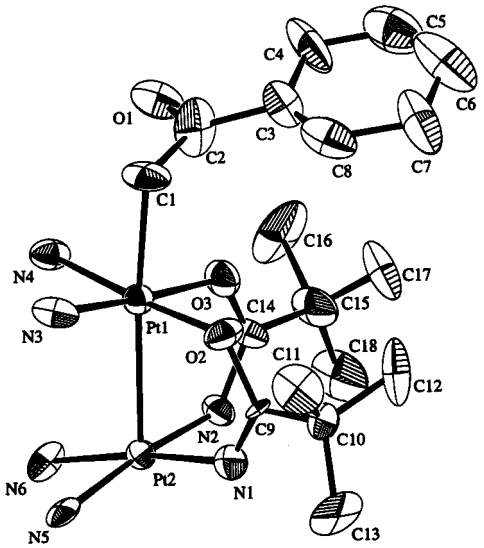


Figure 1. ORTEP drawing of complex **4**·$PhCOCH_3$. Thermal ellipsoids are drawn at the 30% probability level.

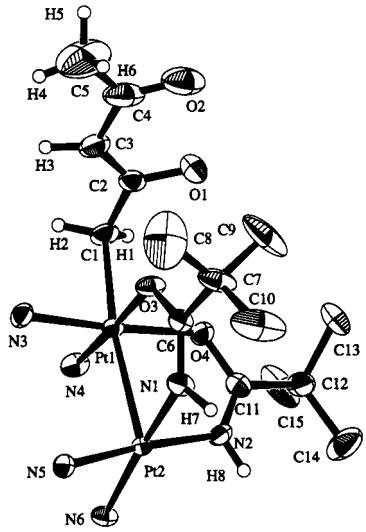


Figure 2. ORTEP drawing of complex **6**. Thermal ellipsoids are drawn at the 30% probability level.

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Table 1. Selected Bond Distances (Å) of Complexes **4**·$PhCOCH_3$ and **6**

	4·$PhCOCH_3$	**6**
Pt(1)−Pt(2)	2.676(1)	2.7206(6)
Pt(1)−O(2)	2.00(2)	
Pt(1)−O(3)	2.00(2)	2.009(6)
Pt(1)−O(4)		2.019(6)
Pt(1)−N(3)	2.04(2)	2.045(7)
Pt(1)−N(4)	2.06(2)	2.042(7)
Pt(1)−C(1)	2.15(2)	2.114(8)
Pt(2)−N(1)	2.03(2)	2.004(7)
Pt(2)−N(2)	1.98(2)	2.014(7)
Pt(2)−N(5)	2.04(2)	2.069(7)
Pt(2)−N(6)	2.08(2)	2.086(7)
O(1)−C(2)	1.27(3)	1.30(1)
O(2)−C(4)		1.26(2)
C(1)−C(2)	1.48(4)	1.46(1)
C(2)−C(3)	1.49(4)	1.39(1)
C(3)−C(4)	1.41(5)	1.44(2)
C(3)−C(8)	1.41(5)	
C(4)−C(5)	1.40(6)	1.52(2)
C(5)−C(6)	1.43(6)	
C(6)−C(7)	1.40(6)	
C(7)−C(8)	1.51(5)	

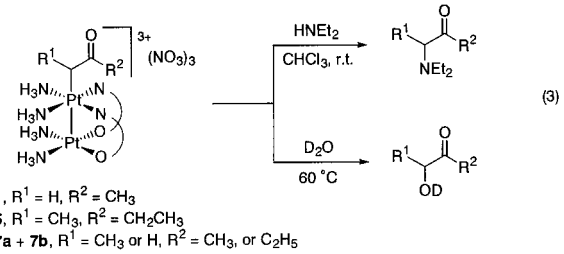
Table 2. Selected Bond Angles (deg) of Complexes **4**·$PhCOCH_3$ and **6**

	4·$PhCOCH_3$	**6**
Pt(2)−Pt(1)−C(1)	173.6(9)	172.3(3)
Pt(1)−C(1)−C(2)	106(2)	112.4(6)
O(1)−C(2)−C(1)	117(3)	116.5(9)
O(1)−C(2)−C(3)	113(3)	121.8(10)
O(2)−C(4)−C(3)		119(1)
O(2)−C(4)−C(5)		120(1)
C(1)−C(2)−C(3)	129(3)	121.7(9)
C(2)−C(3)−C(4)	116(3)	119(1)
C(3)−C(4)−C(5)	111(4)	120(1)

cis form of the two carbonyl oxygen atoms in the diketonyl group is stabilized by the formation of hydrogen bonding between the two oxygen atoms in its enol form, which is also reflected in the planar structure of the diketonyl group (see Supporting Information). The enolic form of the β-diketone forming hydrogen bonding has been observed in the acetylacetonato−Pt(II) complex having a platinum−olefinic bond.[26] The two hydrogen atoms bound to the nitrogen atoms of the two pivalamidate ligands of complex **6** were located in the final electron density map of the difference Fourier synthesis, and therefore the head-to-head (H−H) coordination mode of the two pivalamidate bridging ligands was confirmed.[23]

It should be noted that all the ketonyl complexes prepared in the present study have one ketonyl axial ligand at one Pt(III) atom, and the other end of the Pt(III)−Pt(III) axis is not coordinated by any ligands. This is in contrast to the previously reported acetonyl complex **1**, in which the other terminal of the Pt−Pt axis is very loosely coordinated by a nitrate oxygen with the Pt−O distance of 2.667 Å.[3] The selected bond lengths and bond angles of complexes **4** and **6** are listed in Tables 1 and 2.

Reactions of Ketonyl−Pt(III) Complexes with $HNEt_2$ and H_2O. It is well-known that the alkyl−transition metal complexes usually tend to react with an electrophile, such as acids and halogens etc.[27] The ketonylplatinum(III) complex can, however, receive a nucleophilic attack on the carbon atom bound to the Pt(III) atom and release the corresponding nucleophile-substituted ketones. In the previous communucation, the reactions of the acetonyl−Pt(III) complex **1** with NaOH and NaBr were reported to produce the corresponding nucleophile-substituted acetones.[3] In the present study, $HNEt_2$, NaOH, and H_2O were found to react similarly to the ketonyl−Pt(III) complexes. Treatment of acetonyl complex **1** with $HNEt_2$ in $CHCl_3$ at room temperature generated aminoacetone quantitatively (eq 3). Complex **1** was completely decomposed to release



(3)

1, R^1 = H, R^2 = CH_3
5, R^1 = CH_3, R^2 = CH_2CH_3
7a + **7b**, R^1 = CH_3 or H, R^2 = CH_3, or C_2H_5

hydroxy-substituted acetone in water at 60 °C (eq 3). Complex **5** was reacted with nucliophile to give the corresponding nucleophile-substituted products in a moderate yield as expressed in eq 3. Only 1-diethylamino-2-butanone was detected in the reaction of the mixture of **7a** and **7b** with $HNEt_2$ in a low conversion; however, 3-hydroxy-2-butanone together with a small amount of 1-hydroxy-2-butanone were found in the decomposition of the mixture in water. Such low conversion in the reaction of the bulkier ketonyl group with $HNEt_2$ and H_2O is in contrast to the moderate to high yield of the acetonyl−Pt(III) reaction with water,[3] and indicates that the nucleophilic attack may take place through a S_N2 mechanism. The high electrophilicity of the ketonylplatinum(III) complexes can be accounted for by the high electron-withdrawing ability of the Pt(III) atom. Such high electrophilicity is also observed in the double nucleophilic attacks successively occurring on the two carbon atoms of an olefinic double bond first realized on a Pt-$(III)_2$ complex. The reaction gave the corresponding dinucleophile-dubstituted alkanes, in which the second nucleophilic attack occurs to the carbon atom bound to the Pt(III) atom.[19] Nucleophilic attack on alkyl−platinum(IV) complexes has been reported previously.[28] In addition, electrophilic property is reported also for an alkyl−Pt(II) complex bearing a strong electron-withdrawing group in the ligand[29] and a methyl−Hg(II) complex.[10a] The reactivity of the ketonyl−Pt(III) complexes toward nucleophiles provides a new route for the synthesis of α-amino- and α-hydroxy-substituted ketones. In these reactions, the Pt(III) complex is reduced and $[Pt^{II}_2(NH_3)_4(pivalamidate)_2]^{2+}$ is released.

Mechanistic Studies. As proposed in Scheme 1, there are several possible pathways which can lead to ketonylplatinum(III) dinuclear complex. To examine and clarify the real process that operates in the reaction of platinum blue complex with ketones, we carried out the following experiments.

Addition of acetone to the Pt(III) dimeric complex **3** prepared in situ by oxidation of Pt(II)/Pt(III) mixed valent platinum blue complex **2** with $Na_2S_2O_8$ in water gave acetonylplatinum(III) dinuclear complex **1**. This reaction indicates that the C−H bond activation of acetone is promoted by a Pt(III) atom rather than Pt(II), and route a in Scheme 1, oxidative addition of an α-C−H

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Table 3. Reaction of Platinum Blue Complex **2** with Butanone in Various Conditions[a]

entry	condition	molar ratio[b] **7a**/**7b**	total yield[b] (**7a** + **7b**), %
1	Hg lamp light	2.5	56
2	room light	1.7	65
3	dark	1.1	68
4	dark with 2,4,6-tri-*tert*-butylphenol (10 equiv)	0.1	72

[a] Reaction conditions: A mixture of platinum blue complex (0.01 mmol), butanone (1 mL), and concentrated HNO_3 (0.2 mL) was stirred for 16 h at room temperature under light or dark as indicated in the table. [b] The molar ratios of **7a** to **7b** and total yields were determined by ^{1}H NMR spectroscopy.

bond to a Pt(II) atom, can be excluded. Similarly, crystals of acetophenonyl and acetylacetonyl complexes, **4** and **6**, have also been obtained from the reaction of **3** with the corresponding ketones in aqueous solution.

To identify the real reaction pathway, 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 ^{16}O isotope exclusively. 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 our previous study, both hydrocyethlene π-complex and its deprotonated β-ketonyl complex were observed in equilibrium in the ^{1}H NMR spectrum of the aqueous solution.[18] In the present experiment, however, no such π-complex of the coordinated enol was observed. 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 to 1 in the reaction of the Pt(III) complex **3** with butanone in the presence of concentrated nitric acid at room temperature under room light. This may indicate a competition between 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 as summarized in Table 3. Change of the light source from room light to a mercury lamp rises the **7a**/**7b** ratio (entry 1, Table 3), whereas the ratio decreases when the reaction is carried out in the dark (entry 3), and drops markedly when a radical trapping agent, 2,4,6-tri-*tert*-butylphenol, is added (entry 4). These results strongly support that the complex **7a** is formed via a radical mechanism, in which the $CH_3COCH{\cdot}(CH_3)$ radical can be the intermediate. An electron-transfer mechanism has been proposed in the photoreactions of $PtCl_6^{2-}$ in acetone to give acetonyl−Pt(IV) complex, or in the reaction of $PtCl_6^{2-}$ in *n*-alkanes.[5a,16,30] In the latter reaction, a Pt(III) species was detected by ESR spectroscopy as the intermediate. A radical mechanism has also been proposed in the formation of the Rh−CH_2COCH_3 complex.[31] The fact that the presence of a radical trapping agent does not suppress the formation of complex **7b** strongly suggests that **7b** is formed via a different mechanism. The electrophilic displacement as shown in route a (Scheme 1) would be 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.[4−6] The yields decrease slightly when the reactions are carried out under light (entries 1 and 2, Table 3), which can be due to the radical side reactions.

The competitive processes were further observed in the reactions of platinum blue complex **2** with a mixture of acetone and 3-pentanone in the presence of concentrated HNO_3. Under room light, the reaction gives a mixture of acetonyl complex **1** and pentanonyl−Pt(III) complex **5** in a 3 to 1 molar ratio. The amount of complex **1** is increased whereas formation of complex **5** is markedly suppressed when the reaction is carried out in the dark with the addition of a radical trapping agent. The result again indicates that the activation of a secondary C−H bond mainly occurs via a radical process, whereas an electrophilic displacement mechanism is predominant for a primary C−H bond. In the reaction with 3-methyl-2-butanone, the reaction proceeds exclusively to the primary C−H bond in the α-position, which reflects that the steric effect operates significantly in determining the reaction position.

Conclusions

Various ketonylplatinum(III) complexes were synthesized by the reaction of the corresponding ketones with platinum blue complex **2** in the presence of an oxidant. The method provides a general means for the preparation of the ketonyl−Pt(III) compounds. Competitive mechanisms of the radical process and the electrophilic displacement have been observed directly in the reaction of platinum blue complex with butanone in the presence of nitric acid which gave two types of ketonylplatinum(III) dinuclear complexes—one corresponding to the two reaction pathways. The electrophilicity of the ketonylplatinum(III) complexes was found in the reactions with several nucleophilics, and provides a new synthetic process for nucleophile-substituted ketones.

Experimental Section

The NMR spectra were recorded on a JEOL Lambda 270 spectrometer, operating at 270 MHz for ^{1}H and 57.9 MHz for ^{195}Pt and on a Bruker Avance 600 spectrometer operating at 150.9 MHz for ^{13}C. The chemical shifts are reported in δ units (ppm) downfield from Me_4Si for ^{1}H, from Na_2PtCl_6 (external reference, 0 ppm) and K_2PtCl_4 (external reference, −1624 ppm) for ^{195}Pt, and from $Me_3Si(CH_2)_3SO_3Na$ (external reference, 0 ppm) for ^{13}C. In spit of our effort, some carbonyl ^{13}C signals were not observed due to low intensity. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II Elemental Analyzer. Mass spectra were obtained on a JEOL AUTOMASS spectrometer. The IR spectra were recorded for KBr disk samples on a HITACHI I-3000 spectrometer. Ketones, solvents, and amine were used as commercially available. The platinum blue complex **2**[15] and dinuclear acetonylplatinum(III) complex **1**[3] were synthesized as reported in the literature.

Preparation of $[Pt_2((CH_3)_3CCONH)_2(NH_3)_4(CH_2COPh)](NO_3)_3$ (4). General Procedure. In a typical experiment, to a mixture of platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (0.050 g, 0.0307 mmol) and acetophenone (1 mL) was added concentrated nitric acid (0.2 mL). After the mixture was stirred for 16 h at room temperature, yellow precipitate was obtained. Filtration gave yellow solid, which was washed by acetone (2 mL), water (0.5 mL), and acetone (2 × 1 mL) and dried under vacuo to afford **4** as a yellow power (0.040 g, 67%). ^{1}H NMR (D_2O, δ, 270 MHz, 293 K) 8.03 (d,

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J = 7.5 Hz, 2H, Ph), 7.62 (t, J = 7.3 Hz, 1H, Ph), 7.46 (t, J = 7.3 Hz, 2H, Ph), 5.43 (s, $^2J_{Pt-H}$ = 76, $^3J_{Pt-H}$ = 19 Hz, 2H, $PtCH_2CO$), 1.04 (s, 18H, 2Me_3CCONH). $^{13}C\{^1H\}$ NMR (D_2O, δ, 150.9 MHz, 293 K): 203.9 (CH_2COPh), 193.7 (C*C*ONH), 137.3 (*ipso*-C_6H_5,), 129.5 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 134.9 (*p*-C_6H_5), 39.7 (Me_3CCO), 30.5 (Pt*C*H_2-CO), 26.8 (Me_3CCO). Anal. Calcd for $C_{18}H_{39}N_9O_{12}Pt_2$: C, 22.43; H, 4.08; N, 13.08. Found: C, 22.59; H, 4.01; N, 12.93.

The same procedure as described for the preparation of complex **4** was employed for the preparation of complexes **5**−**8**. The ^1H NMR data and elemental analyses are given below:

5: Yield: 65%. ^1H NMR (D_2O, δ, 270 MHz, 293 K): 5.38 (q, J = 6.6 Hz, $^2J_{Pt-H}$ = 82 Hz, 1H, PtC*H*CH_3), 2.69 (dq, J = 19.6, 6.8 Hz, 1H, $CH_3CHH'CO$), 2.47 (dq, J = 19.8, 6.9 Hz, 1H, $CH_3CHH'CO$), 1.02 (s, 9H, Me_3CCONH), 0.97 (s, 9H, Me_3CCONH), 0.88 (t, J = 6.7 Hz, 3H, $CH_3CHH'CO$), 0.06 (d, J = 6.8 Hz, $^3J_{Pt-H}$ = 32 Hz, 3H, $PtCHCH_3$). $^{13}C\{^1H\}$ NMR (D_2O, δ, 150.9 MHz, 293 K): 53.8 (Pt*C*HCO), 40.0 (*C*CONH), 35.8 ($COCH_2CH_3$), 26.8 (Me_3CCONH), 18.6 ($PtCHCH_3$), 6.7 ($COCH_2CH_3$). Anal. Calcd for $C_{15}H_{41}N_9O_{12}Pt_2$: C, 19.38; H, 4.45; N, 13.56. Found: C, 19.09; H, 4.22; N, 13.22.

6: Yield 58%. ^1H NMR (D_2O, δ, 270 MHz, 293 K): 5.54 (s, 0.5H, COCHCO),[32] 4.85 (s, $^2J_{Pt-H}$ = 77 Hz, 2H, $PtCH_2$), 2.19 (s, 3H, CH_3), 1.03 (s, 18H, 2Me_3CCONH). $^{13}C\{^1H\}$ NMR (D_2O, δ, 150.9 MHz, 293 K): 76.4 (CO*C*H2CO), 39.9 (Me_3*C*CONH), 39.2 (Pt*C*H2CO), 30.5 ($COCH_3$), 27.3 (Me_3CCONH). Anal. Calcd for $C_{15}H_{40}N_9O_{13}Pt_2$: C, 19.07; H, 4.27; N, 13.34. Found: C, 19.07; H, 4.12; N, 13.07. IR: $\upsilon_{C=O}$ 1602 cm^{-1}.

7a + **7b** (molar ratio 1.7/1): Yield 62%. ^1H NMR for **7a** (D_2O, δ, 270 MHz, 293 K): 5.39 (q, J = 6.7 Hz, $^2J_{Pt-H}$ = 78 Hz, 1H, PtC*H*CH_3), 2.25 (s, 3H, CH_3CO), 1.05 (s, 9H, Me_3CCONH), 1.02 (s, 9H, Me_3-CCONH), 0.11 (d, J = 6.9 Hz, $^3J_{Pt-H}$ = 30 Hz, 3H, $PtCHCH_3$). ^1H NMR for **7b** (D_2O, δ, 270 MHz, 293 K): 4.86 (s, $^2J_{Pt-H}$ = 76 Hz, $^3J_{Pt-H}$ = 18 Hz, 2H, $PtCH_2$), 2.58 (q, J = 6.3 Hz, 2H, CH_2CH_3), 1.10 (s, 18H, 2Me_3CCONH), 0.94 (t, J = 6.1 Hz, 3H, CH_2CH_3). $^{195}Pt\{^1H\}$ NMR for **7a** + **7b** (D_2O, δ, 57.94 MHz, 293 K): −101.3 (s, $^1J_{Pt-Pt}$ = 3171 Hz, PtN_2O_2), −1931.1 (s, $^1J_{Pt-Pt}$ = 3171 Hz, PtN_4). Anal. Calcd for $C_{15}H_{40}N_9O_{13}Pt_2$ (**7a** + **7b**): C, 18.36; H, 4.29; N, 13.77. Found: C, 17.97; H, 4.07; N, 13.62. IR: $\upsilon_{C=O}$ 1598 cm^{-1}. The quality of the $^{13}C\{^1H\}$ NMR spectra for the mixture of **7a** with **7b** was not suitable for complete assignment of each component. Therefore, the $^{13}C\{^1H\}$ NMR data were omitted.

8: Yield: 59%. ^1H NMR (D_2O, δ, 270 MHz, 293 K): 4.92 (s, $^2J_{Pt-H}$ = 76 Hz, 2H, $PtCH_2$), 2.66 (sept, J = 7.1 Hz, 1H, CH), 1.06 (d, J = 7.0 Hz, 6H, CH_3, overlapped with the signal of pivalamidate anion), 1.02 (s, 18H, 2Me_3CCONH). $^{13}C\{^1H\}$ NMR (D_2O, δ, 150.9 MHz, 293 K): 139.7 (Me_3C*C*ONH), 42.8 (CO*C*HMe_2), 39.9 (Me_3*C*CONH), 32.7 (Pt*C*H_2CO), 27.0 (Me_3CCONH), 17.2 (COCH*C*H_3). Anal. Calcd for $C_{15}H_{41}N_9O_{12}Pt_2$: C, 19.38; H, 4.45; N, 13.56. Found: C, 18.64; H, 4.53; N, 13.46.

Method for the Preparation of Crystals of 4·PhCOCH$_3$ and 6. To a solution of platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (**2**) (0.010 g, 0.00615 mmol) in water (0.5 mL) was added $Na_2S_2O_8$ (0.003 g, 0.012 mmol). The mixture was stirred for 10 min at room temperature to give a yellow solution. Addition of concentrated HNO_3 (0.10 mL) and acetophenone (0.10 mL) to the yellow solution and letting the mixture stand for a few days at room temperature gave yellow crystals of **4**·$PhCOCH_3$. Use of acetylacetone instead of acetophenone gave yellow crystals of **6**. Both crystals were used for the X-ray diffraction analysis.

Reactions of Ketonylplatinum(III) Dinuclear Complexes with HNEt$_2$. General Procedure. In a typical experiment, to a suspension of acetonyl diplatinum(III) complex **1** (0.018 g, 0.02 mmol) in $CHCl_3$ (1 mL) was added $HNEt_2$ (0.041 mL, 0.40 mmol) at room temperature. After the mixture was stirred for 2 h, a yellowish orange precipitate formed and was filtered. The pale yellow filtrate was evaporated to dryness and analyzed by ^1H NMR in $CDCl_3$ and GC-MS to contain $CH_3COCH_2NEt_2$ as the exclusive decomposition product of the acetonyl group. The product was confirmed by comparison of the spectrum with that of the standard sample.

(32) The signal for methylene protons between two carbonyl groups was observed in less intensity, probably due to the exchange between the enol-form proton and the deuterium of the solvent D_2O.

The same procedure as described above for the reaction of complex **1** with $HNEt_2$ was used in the reactions of complexes **5** and **7** with $HNEt_2$. 2-Diethylamino-3-pentanone was obtained in the reaction with complex **5** in 57% conversion together with a small amount of unidentified compounds as confirmed by ^1H NMR and GC-MS. ^1H NMR ($CDCl_3$, δ, 270 MHz, 293 K): 3.31 (q, J = 7 Hz, 1H, H^2), 2.66 (q, J = 7 Hz, 4H, $N(CH_2CH_3)_2$), 2.53 (q, J = 7 Hz, 2H, H^4), 1.2 (d, J = 7 Hz, 3H, H^1), 1.14 (t, J = 7 Hz, 6H, $N(CH_2CH_3)_2$), 1.02 (t, J = 7 Hz, 3H, H^5). MS (EI) m/z (relative intensity) 157 (M^+, 2), 142 (23), 129 (16), 100 (20), 85 (67), 72 (19), 58 (100). 1-Diethylamino-2-butanone was obtained in the reaction with complex **7** in 23% conversion as analyzed by ^1H NMR and GC-MS together with some unidentified compounds. ^1H NMR ($CDCl_3$, δ, 270 MHz, 293 K): 3.29 (s, 2H, H^1), 2.62 (q, J = 7 Hz, 4H, $N(CH_2CH_3)_2$), 2.51 (q, J = 7 Hz, 2H, H^3), 1.2 (t, J = 7 Hz, 6H, $N(CH_2CH_3)_2$, overlapped with the signal of the impurity), 1.05 (t, J = 7 Hz, 3H, H^4). MS (EI) m/z (relative intensity), 128 (M^+ − Me, 3), 115 (5), 101 (8), 84 (12), 73 (48), 58 (100).

Reactions of Ketonylplatinum(III) Dinuclear Complexes with Water. General Procedure. In a typical experiment, a solution of acetonyl diplatinum(III) complex **1** (0.018 g, 0.02 mmol) in D_2O (0.6 mL) was warmed to 60 °C for 20 h to give a dark blue solution. The ^1H NMR and GC-MS analysis revealed that the acetonyl group of **1** was completely converted to hydroxyacetone, which was confirmed by comparison with the standard sample. The same product was obtained when diluted NaOH solution (0.01 M) was added instead of D_2O.

The same procedure for the thermal decomposition of complex **1** in D_2O was used in the thermal decomposition of complexes **5** and **7**. 2-Hydroxy-3-pentanone was obtained in the decomposition of complex **5** in 60% conversion as confirmed by ^1H NMR and GC-MS. ^1H NMR (D_2O,δ, 270 MHz, 293 K): 4.23 (q, J = 7 Hz, 1H, H^2), 2.40 (q, J = 7 Hz, 2H, H^4), 1.17 (d, J = 7 Hz, 3H, H^1), 1.0 (t, J = 7 Hz, 3H, H,[5] overlapped with the signal of the impurity). MS (EI) m/z (relative intensity) 103 (M^+, 21), 88 (12), 69 (6), 57 (100). 3-Hydroxy-2-butanone in 35% conversion and a small amount of 1-hydroxy-2-butanone were obtained in the decomposition of complex **7**, which was confirmed by comparison of the ^1H NMR spectra with those of the standard samples, together with unidentified compounds.

Mechanistic Studies. (a) Reaction of Pt(III)$_2$ complex with acetone: To a solution of platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (**2**) (0.016 g, 0.01 mmol) in H_2O (0.5 mL) was added $Na_2S_2O_8$ (0.005 g, 0.02 mmol). The mixture was stirred for 20 min at room temperature to give a yellow solution of $Pt(III)_2$ complex. Addition of concentrated HNO_3 (0.1 mL) and acetone (0.5 mL) and stirring for 5 h at room temperature gave yellow precipitate, which was filtered and confirmed to be acetonyl complex **1** by ^1H NMR and elemental analysis.

(b) Formation of acetonylplatinum(III) complex 1 in the presence of $H_2{}^{18}O$ and its reaction with HNEt$_2$: To a mixture of platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (**2**) (0.016 g, 0.01 mmol) and $H_2{}^{18}O$ (0.02 mL) was added acetone (1 mL) and HNO_3 (0.2 mL). The mixture was stirred for 20 h at room temperature to give yellow precipitate, which was filtered, washed by acetone, and dried. The resulting yellow solid was suspended in $CHCl_3$ (0.5 mL) and $HNEt_2$ (0.02 mL, 0.20 mmol) was added. After the mixture was stirred for 3 h, the precipitate was filtered off and the filtrate was analyzed by GC-MS, which indicated that $CH_3C^{16}OCH_2NEt_2$ is formed exclusively. MS (EI) m/z (relative intensity) 129 (M^+, 2), 114 (1), 86 (100), 85 (25), 58 (22).

Addition of $Na_2S_2O_8$ (0.012 g, 0.05 mmol) instead of the oxidant HNO_3 and prolonged reaction time to 3 days gave the same result as above.

(c) Reactions of platinum blue complex with butanone in different conditions. General procedure. To a suspension of platinum blue complex $[Pt_4((CH_3)_3CCONH)_4(NH_3)_8](NO_3)_5$ (**2**) (0.016 g, 0.01 mmol) in butanone (1 mL) was added HNO_3 (0.2 mL) at room temperature. The mixture was stirred in room light for 16 h to give a yellow precipitate, which was filtered, washed by acetone (3 × 1 mL), and dried under vacuo. The yellow powder thus formed was dissolved completely in D_2O (about 1 mL) and MeOH (0.004 mL, 0.10 mmol) was added as an internal reference. The solution was analyzed by ^1H

NMR spectroscopy to contain complexes **7a** and **7b** in a molar ratio of 1.7 to 1 (total yield: 62% based on ^{1}H NMR).

The same procedure as described above for the reaction under room light was employed for the reactions in different conditions as shown in Table 1.

(d) Competitive reactions of acetone and 3-pentanone toward the Pt(III)$_2$ dimeric complex. To a mixture of platinum blue complex (0.016 g, 0.01 mmol), acetone (0.5 mL), and 3-pentanone (0.5 mL) was added concentrated HNO_3 (0.2 mL). The reaction mixture was stirred at room temperature for 16 h under room light. The yellow precipitate formed was filtered, washed with acetone (3 × 1 mL), and dried, then analyzed by ^{1}H NMR spectroscopy to contain a mixture of complex **1** and **5** in a molar ratio of 3 to 1 (total yield: 63%, based on ^{1}H NMR spectra by using MeOH as the internal reference).

The same competitive reaction was carried out in the presence of 2,4,6-tri-*tert*-butylphenol (0.026 g, 0.1 mmol) in the dark. A mixture of **1** and **5** was obtained in a ratio of 8 to 1 (total yield: 71%).

Crystal Structure Determination of 4 and 6. Yellow crystals of **4**·$PhCOCH_3$ and **6** suitable for X-ray diffraction analysis were coated with epoxy resin for use in the X-ray diffraction study. Intensity data were collected on a Rigaku AFC-7R diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 25 °C. Three standard reflections were measured after 150 reflections. During the date collection of complex **4**, the standard intensities decreased by 14.4% on average. A linear correction factor was applied to the data for **4**·$PhCOCH_3$. No decay correction was applied in **6**, since significant crystal deterioration was not observed. Empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.53 to 1.00 (**4**·$PhCOCH_3$) and from 0.51 to 1.00 (**6**). The data were corrected for Lorentz and polarization effects in both crystals. Further details of the data collection procedures are summarized in Table 4 and in the Supporting Information.

Structures of both **4**·$PhCOCH_3$ and **6** were solved by the heavy-atom Patterson methods and refined by using the crystal analysis package teXsan. All non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of **4**·$PhCOCH_3$ were not included in the calculation. In complex **6**, the hydrogen atoms in the diketonyl group and the two H atoms bound to the nitrogen atoms in the pivalamidate ligand were found in the electron density maps, which were included in the calculation but were not refined. The final cycle of the full-matrix least-squares refinement based on 3390 observed reflections ($I > 2.5\sigma(I)$) and 451 parameters converged to the *R* and *Rw* values of 0.068 and 0.072 for **4**·$PhCOCH_3$. Those for **6** with 5044 observed reflections ($I > 3.00\sigma(I)$) and 352 parameters were 0.033 and 0.038. The definitions for *R* and *R*w are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$. The largest peaks in the final difference Fourier syntheses were 1.39 e/Å^3 for **4**·$PhCOCH_3$, in which the largest is close to the Pt atom (<1 Å), and 0.78 e/Å^3 for **6**. The final atomic positional and thermal parameters and the interatomic distances and angles for **4**·$PhCOCH_3$ and **6** are given in the Supporting Information.

Table 4. Summary of Crystal Data for Complexes **4**·$PhCOCH_3$ and **6**

	4·$PhCOCH_3$	**6**
formula	$C_{26}H_{47}N_9O_{13}Pt_2$	$C_{15}H_{39}N_9O_{19}Pt_2$
fw	1083.89	943.71
cryst system	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	10.133(2)	10.105(2)
b (Å)	9.684(2)	17.225(3)
c (Å)	38.10(1)	9.522(2)
α (deg)		104.50(1)
β (deg)	90.86(2)	96.90(2)
γ (deg)		73.07(2)
V (Å^3)	3738(1)	1533.1(5)
T (deg)	25 ± 1	25 ± 1
Z	4	2
ρ_{calcd} (g cm^{-3})	1.926	2.044
crystal dimens (mm^3)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.10
absorp coeff (cm^{-1})	75.17	91.47
2*θ* range (deg)	5 < 2*θ* < 55	5 < 2*θ* < 55
residual electron den (e/Å^3)	1.39	0.78
no. of obsd unique data	3390 ($I > 2.5\sigma(I)$)	5044 ($I > 3\sigma(I)$)
no. of params	451	352
R^a	0.068	0.033
$R_w{}^b$	0.072	0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Supporting Information Available: X-ray data for **4**·$PhCOCH_3$ and **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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