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Reactions of a Platinum(III) Dimeric Complex with Alkynes in Water: Novel Approach to α-Aminoketone, α-Iminoketone, and α,β-Diimine via Ketonyl−Pt(III) Dinuclear Complexes

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Abstract: Reaction of the platinum(III) dimeric complex $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(NO_3)_2](NO_3)_2$ (**1**), prepared in situ by the oxidation of the platinum blue complex $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ (**2**) with $Na_2S_2O_8$, with terminal alkynes CH≡CR (R = $(CH_2)_nCH_3$ ($n = 2-5$), $(CH_2)_nCH_2OH$ ($n = 0-2$), CH_2OCH_3, and Ph), in water gave a series of ketonyl−Pt(III) dinuclear complexes $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH_2-COR)](NO_3)_3$ (**3**, R = $(CH_2)_2CH_3$; **4**, R = $(CH_2)_3CH_3$; **5**, R = $(CH_2)_4CH_3$; **6**, R = $(CH_2)_5CH_3$; **7**, R = CH_2OH; **8**, R = CH_2CH_2OH; **9**, R = $(CH_2)_2CH_2OH$; **10**, R = CH_2OCH_3; **11**, R = Ph). Internal alkyne 2-butyne reacted with **1** to form the complex $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH(CH_3)COCH_3)](NO_3)_3$ (**12**). These reactions show that Pt(III) reacts with alkynes to give various ketonyl complexes. Coordination of the triple bond to the Pt(III) atom at the axial position, followed by nucleophilic attack of water and hydrogen shift from the enol to keto form, would be the mechanism. The structures of complexes **3**·H_2O, **7**·$0.5C_3H_4O$, **9**, **10**, and **12** have been confirmed by X-ray diffraction analysis. A competitive reaction between equimolar 1-pentyne and 1-pentene toward **1** produced complex **3** and $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH_2CH(OH)CH_2CH_2CH_3)]-(NO_3)_3$ (**14**) at a molar ratio of 9:1, suggesting that alkyne is more reactive than alkene. The ketonyl−Pt(III) dinuclear complexes are susceptible to nucleophiles, such as amines, and the reactions with secondary and tertiary amines give the corresponding α-amino-substituted ketones and the reduced Pt(II) complex quantitatively. In the reactions with primary amines, the once formed α-amino-substituted ketones were further converted to the iminoketones and diimines. The nucleophilic attack at the ketonyl group of the Pt(III) complexes provides a convenient means for the preparation of α-aminoketones, α-iminoketones, and diimines from the corresponding alkynes and amines.

Introduction

Although Pt(III)−Pt(III) complexes having various bridging ligands such as amidates,[1-3] pyrimidines,[1-9] other nitrogen donor ligands,[1,10] sulfur-containing ligands,[1,4,5,11] acetates,[1,4,5,12] pyrophosphites,[13] phosphates,[1,4,5,13,14] sulfates,[1,5,14,15] and σ-carbon-containing ligands,[1,16,17] and the Pt(III)−Pt(III) complex without bridging ligands[18] have been established as a new class of high-valent platinum compounds, organoplatinum(III) chemistry still remains to be explored. Just one mononuclear organo-platinum(III) complex has been reported, but its reactivity is not well-known.[19] Dinuclear platinum(III) complexes having an alkyl group at the axial position of the Pt(III)−Pt(III) bond are relatively rare, and only two had been known before our

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Scheme 1
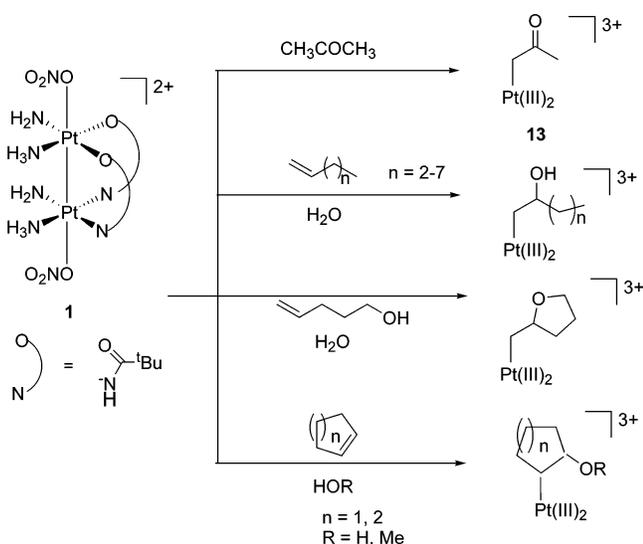
extensive study was started on the reactions of dinuclear Pt(III) complexes with olefins: oxidative addition of methyl iodide to the dinuclear pyrophosphite-bridged Pt(II) complex $K_4[Pt_2(P_2O_5H_2)_4]$, giving the Pt(III) complex $K_4[Pt_2(P_2O_5H_2)_4\text{-}MeI]$ with the methyl group at the axial position,[20] and the platinum(III) compound $[Pt_2(NH_3)_4(C_5H_5N_2O_2)_3](SiF_6)(NO_3)\cdot7H_2O$ having 1-methyluracilate as both bridging and axial ligands[21] are the early rare examples of Pt(III)−C bonds at the axial site.

Following the above two examples, the pivalamidate-bridged platinum(III) dimeric complex $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(NO_3)_2](NO_3)_2$ (**1**) was found to react with acetone to give a novel axial acetonyl−Pt(III)$_2$ complex via C−H bond activation of acetone (Scheme 1).[22] Compound **1** is generated in situ by the oxidation of the platinum blue complex $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ (**2**) with HNO$_3$. A general method for the synthesis of ketonyl−platinum(III) complexes was developed recently for various ketones.[23]

The chemistry of organoplatinum(III) dinuclear complexes having pivalamidate bridging ligands has been further developed by the finding that various olefins react with **1**. Compound **1** reacts with linear terminal olefins in water to give β-hydroxy-alkyl−Pt(III) complexes, and reaction of **1** with 4-penten-1-ol gives the 2-methyltetrahydrofurfuryl complex as shown in Scheme 1.[24] Novel alkyl−Pt(III) complexes are also afforded by the reactions with cyclic olefins in water or methanol (Scheme 1).[25] Axial coordination of the olefinic double bond to one of the two platinum(III) atoms in **1**, followed by intra- or intermolecular nucleophilic attack, is proposed as the reaction mechanism. Interestingly, the α-carbon atom on the Pt(III) atom further undergoes the second nucleophilic attack, and consecutive double nucleophilic attack has been realized

to the olefins on the Pt(III)$_2$ complex. In aqueous solution, the double nucleophilic attack releases 1,2-dihydroxy addition products. This is a new and very novel process of organoplatinum(III) chemistry.[25]

Although ketonyl−transition-metal complexes had been known,[26] their reactivities such as alkylation reactions have rarely been studied.[27] To our knowledge, the nucleophilic attack of water, halides, and diethylamine on our ketonyl−Pt(III)$_2$ complex is the first example that a ketonyl group on a transition metal undergoes nucleophilic attack.[22,23]

As an extension of our study on the chemistry of organoplatinum(III) complexes, reactions with other unsaturated organic substrates were examined. Here, we report the reaction of complex **1** with alkynes in water to give ketonyl−Pt(III) dinuclear complexes, which is the alternative route to prepare the ketonyl−Pt(III) complex. In the previous report,[22,23] the reaction of the ketonyl−Pt(III) complex was examined with only diethylamine, but in the present study the reaction was studied also with tertiary and primary amines. The ketonyl complexes undergo nucleophilic attack also by secondary and tertiary amines to give amino-substituted ketones. In the reactions with primary amines, the α-aminoketones are further converted to iminoketones and diimines.

Results and Discussion

Reactions of Alkynes with Pt(III)$_2$ Complex 1. Various terminal CH≡CR (R = (CH$_2$)$_n$CH$_3$ (n = 2−5), (CH$_2$)$_n$CH$_2$OH (n = 0−2), CH$_2$OCH$_3$, and Ph) and internal CH$_3$C≡CCH$_3$ alkynes were used in the reactions. Addition of terminal alkynes CH≡CR to an aqueous solution of platinum(III) dimeric complex **1**, prepared in situ by the oxidation of platinum blue complex **2** with Na$_2$S$_2$O$_8$, at room temperature smoothly gave the corresponding dinuclear ketonyl−Pt(III) complexes $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH_2COR)](NO_3)_3$ (**3**, R = (CH$_2$)$_2$CH$_3$; **4**, R = (CH$_2$)$_3$CH$_3$; **5**, R = (CH$_2$)$_4$CH$_3$; **6**, R = (CH$_2$)$_5$CH$_3$; **7**, R = CH$_2$OH; **8**, R = CH$_2$CH$_2$OH; **9**, R = (CH$_2$)$_2$CH$_2$OH; **10**, R = CH$_2$OCH$_3$; **11**, R = Ph) as shown in eq 1. Internal alkyne 2-butyne formed complex $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH(CH_3)COCH_3)](NO_3)_3$ (**12**) (eq 2), which had also been obtained previously from the reaction of **2** with butanone in the presence of concentrated HNO$_3$, via C−H bond activation of the methylene group of butanone.[23] However, this reaction gave a mixture of the 1-butanonyl− and 3-butanonyl−Pt(III) dinuclear complexes formed via C−H activation of the α-methyl and α-methylene group, respectively. In contrast, the 3-butanonyl−Pt(III)$_2$ complex **12** is exclusively obtained in the present reaction of **1** with 2-butyne. In the latter reaction, the water attack at the two possible alkynic carbon atoms π-coordinated to the Pt(III) atom gives an identical compound.
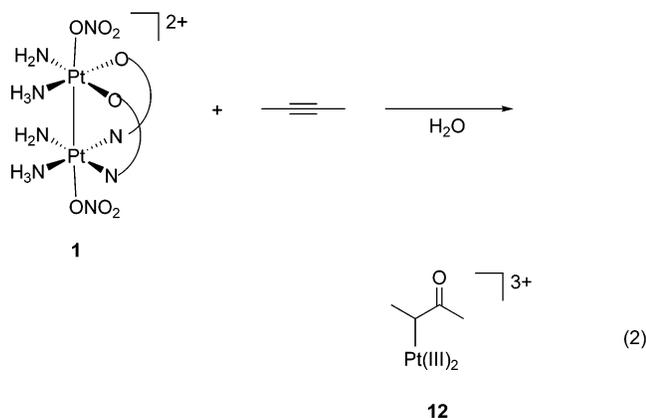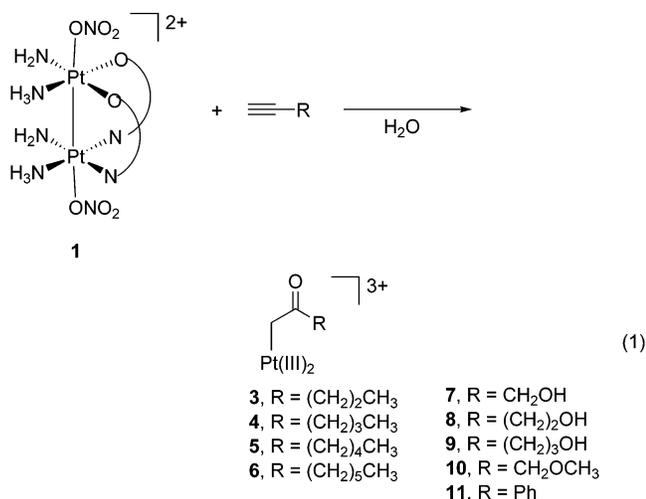
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Table 1. ¹H NMR Data for Complexes **3**−**12**[a]

complex (n, A, B)	H¹ ($^2J_{PtH}$, Hz)	H³ ($^3J_{HH}$, Hz)	H⁴ ($^3J_{HH}$, Hz)	H⁵ ($^3J_{HH}$, Hz)	H⁶ ($^3J_{HH}$, Hz)	H⁷ ($^3J_{HH}$, Hz)	H⁸ ($^3J_{HH}$, Hz)	pivalamidate
3 (3, H, H)	5.01 (s, 79)	2.65 (t, 7.4)	1.65 (m)	0.95 (t, 7.0)				1.18 (s)
4 (4, H, H)	5.13 (s, 78)	2.67 (t, 7.3)	1.61 (m)	1.34 (m)	0.90 (t, 7.0)			1.19 (s)
5 (5, H, H)	5.01 (s, 78)	2.67 (t, 7.5)	1.63 (m)	1.33 (m)	1.22 (m)	0.88 (t, 7.0)		1.20 (s)
6 (6, H, H)	5.02 (s, 78)	2.67 (t, 7.4)	1.64 (m)	1.32 (m)	1.2−1.1 (m)[b]	1.2−1.1 (m)	0.87 (t, 7)	1.20 (s)
7 (1, OH, H)	4.98 (s, 79)[c]	4.21 (s)						1.20 (s)
8 (2, OH, H)	5.03 (s, 79)	2.92 (t, 5.7)	3.93 (t, 5.7)					1.19 (s)
9 (3, OH, H)	5.03 (s, 78)	2.75 (t, 6.9)	1.87 (m)	3.63 (t, 6.7)				1.19 (s)
10[d] (1, OMe, H)	4.90 (s, 73)	4.30 (s)						1.19 (s)
11[e] (0, Ph, H)	5.57 (s, 77)							0.98 (s)
12[f] (1, H, CH₃)	5.52 (q, 78)	2.39 (s)						1.23 (s), and 1.15 (s)[g]

[a] The ¹H NMR spectra were measured in D₂O at room temperature by using Me₄NClO₄ as an internal reference at 3.19 ppm. [b] Overlapped by the signal of the pivalamidate ligands. [c] The integration of the singlet is about 1.5H, probably due to the equilibrium and exchange with the enol form isomer in D₂O solution. [d] The methyl protons of the methoxy group appeared at 3.43 ppm. [e] Protons of the phenyl group: 8.16 (d, J = 7.5 Hz, 2H), 7.75 (t, J = 7.3 Hz, 1H), 7.60 (t, J = 7.3 Hz, 2H). [f] The protons of the methyl group bound to the α-carbon atom appeared at 0.24 ppm (d, $^3J_{HH}$ = 7.02). [g] The two peaks are due to the two optical isomers caused by the chiral center at the α-carbon. The two isomers have been confirmed in the X-ray diffraction analysis.

1

(1)

3, R = (CH₂)₂CH₃   **7**, R = CH₂OH
4, R = (CH₂)₃CH₃   **8**, R = (CH₂)₂OH
5, R = (CH₂)₄CH₃   **9**, R = (CH₂)₃OH
6, R = (CH₂)₅CH₃   **10**, R = CH₂OCH₃
                        11, R = Ph

1

(2)

12

The reaction of **1** with excess 1-pentyne in D₂O was monitored with ¹H NMR spectroscopy, which revealed that the reaction is completed within 10 min at room temperature, and complex **1** is totally converted to the pentanonyl complex **3**. The expected axial π-coordination of 1-pentyne to the Pt(III) atom before the water attack could not be observed, even though the reaction was carried out at 0 °C. No intermediate was observed in the spectra.

All of the complexes obtained were identified by the ¹H NMR spectra and elemental analysis. The ¹H NMR data of complexes

3−**12** are summarized in Table 1, in which the satellite signals are observed for the C1 protons with the coupling constants of 73−79 Hz in all of the complexes. Formation of the ketonyl complexes was also confirmed by the analysis of IR spectra, which gave the characteristic C=O signals of the ketonyl groups (see the Experimental Section). The structures of complexes **3**, **7**, **9**, **10**, and **12** were also confirmed by X-ray diffraction analysis. All of the complexes obtained were the head to head (H−H) isomer in the orientation of the two pivalamidate ligands, and only a signal was observed for the pivalamidate methyl in the ¹H NMR spectra.

Although coordination of the triple bond to the platinum(III) atom could not be observed, formation of the ketonyl−Pt(III) dinuclear complexes suggests that the reaction starts with the coordination of the alkyne triple bond to the N₂O₂-coordinated Pt(III) atom in **1**, which is followed by the nucleophilic attack of water on the triple bond carbon atom and isomerization of the enol to keto form via hydrogen transfer. In the reaction of terminal alkynes, the water attack always takes place on the internal carbon atom of the triple bond. This is the first example of alkyne reaction on a platinum(III) complex, and is contarasted with the well-known Pt(II)−alkyne complexes and their reactivity toward nucleophiles.[28a,b] Similar reactivities were reported on other electrophilic metals such as Hg(II),[28c] Pd(II),[28d] and Au(III).[28e] It is known that high-valent transition metals are less susceptible to unsaturated organic substrates due to the poorer back-donation from the metal center to the unsaturated bond.[29] No platinum(IV)−alkyne complex has been reported except one example: the platinum(IV) complex [PtMe₂(CF₃)(PMe₂Ph)₂]-(PF₆) reacts with 3-butyn-1-ol, HC≡CCH₂CH₂OH, in acetone to give an alkoxyalkyl- or −carbene-type complex.[30] Formation of the ketonyl complexes rather than alkoxyalkyl- or −carbene-

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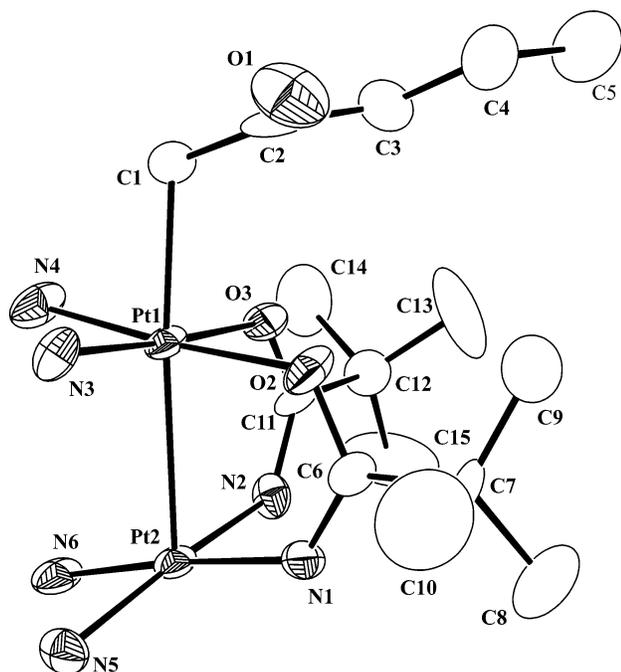(30) Chisholm, M. H.; Clark, H. C. *J. Chem. Soc., Chem. Commun.* **1971**, 1484.

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

type complexes in the reactions of complex **1** with 3-butyn-1-ol and 4-pentyn-1-ol indicates that external nucleophilic attack of water on the triple bond is the more preferable process in our present reaction condition than the intramolecular hydroxy attack as observed previously in the reaction of **1** with 4-penten-1-ol.[24] It is noteworthy that alkynes bearing electron-withdrawing groups, such as HC≡CCOOH and HC≡CCOOEt, did not form the corresponding ketonyl−Pt(III)$_2$ complex.

Structure Analysis of Complexes 3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10, and 12. Yellow crystals of complexes **3·H$_2$O**, **7·0.5C$_3$H$_4$O**, **9**, **10**, and **12** were obtained by addition of 1-pentyne, 2-propyn-1-ol, 4-pentyn-1-ol, methyl propargyl ether, and 2-butyne, respectively, to an aqueous solution of complex **1** prepared in situ by oxidation of complex **2** with Na$_2$S$_2$O$_8$ in aqueous HNO$_3$ solution. The structures were identified by X-ray diffraction analysis. The ORTEP drawings of the cations of complexes **3**, **7**, and **12** are given in Figures 1−3. The ORTEP drawings of complexes **9** and **10** and other crystal data are in the Supporting Information. In complexes **7** and **12**, disorder of the axial ligand is observed, and one (A part) of the two structures is shown in Figures 2 and 3. Both of the disordered structures are also shown in Figures S1 and S4 in the Supporting Information. The refinements of these structures were carried out with the initial occupancy of 0.5 for both components. The final occupancies of the A parts of complexes **7** and **12** were 0.63 and 0.78, respectively. The B parts could not be refined anisotropically, and only isotropical thermal factors were given. No essential difference was observed between the structures of **3** and its hydroxy-substituted complex **9**. The structures of **3**, **7**, **10**, and **12** clearly indicate the formation of the ketonyl−Pt(III) complexes with the axial Pt−C bonds. The bond lengths of Pt−C are 2.105(18) in **3**, 2.097(14) in **7**, 2.088(10) in **10**, and 2.146-(13) Å in **12**. These are slightly shorter (**3**, **7**, and **10**) and slightly longer (**12**) than that in the acetonyl−Pt(III) dinuclear complex [Pt$_2$(NH$_3$)$_4$((CH$_3$)$_3$CCONH)$_2$(CH$_2$COCH$_3$)](NO$_3$)$_3$ (**13**) (2.14 Å).[22] The longer Pt−C bond in **12** may imply the steric hindrance of the bulkier secondary carbon atom bound to the
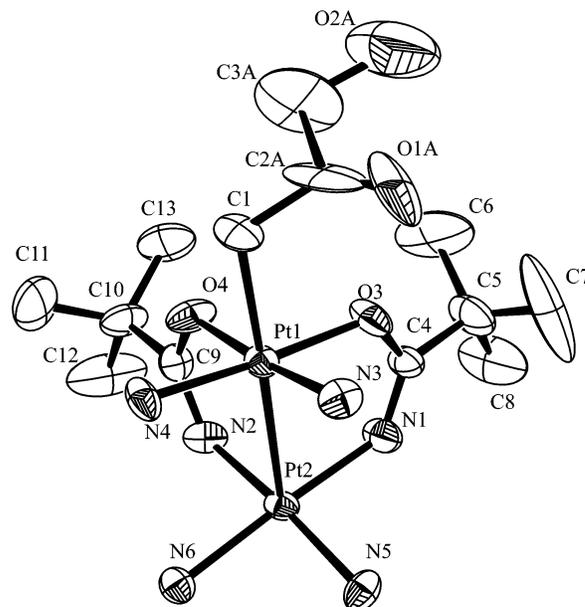

Figure 2. ORTEP drawing of the cation of complex **7**. Thermal ellipsoids are drawn at the 30% probability level.
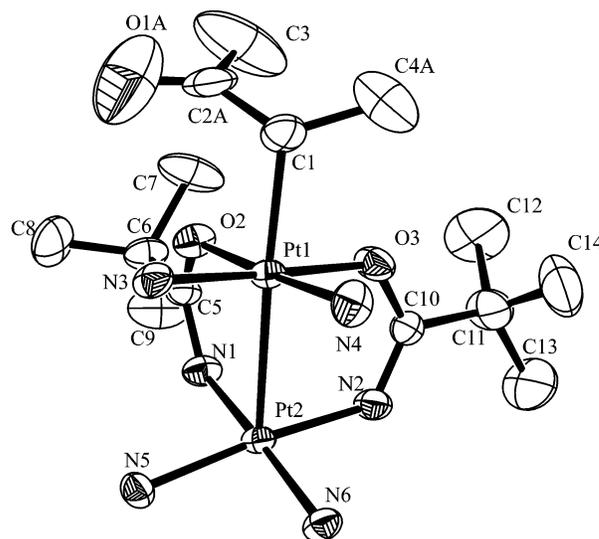

Figure 3. ORTEP drawing of the cation of complex **12**. Thermal ellipsoids are drawn at the 30% probability level.

Pt(III) atom. The C2−O1 bond lengths range from 1.15(7) Å in **7** (C2A−O1A) to 1.24(3) in **12** (C2A−O1A), and all these distances together with the characteristic IR spectra are assigned to C=O double bonds. The C1−C2 bond lengths of all complexes are thought to be appropriate for C−C single bonds. The torsion angles of Pt1−C1−C2−C3 and Pt1−C1−C2−O1 largely deviate from 0° or 180°, indicating that these atoms are not in the same plane. From the above structural parameters, it is suggested that these complexes have a character of the ketonyl form at least in the solid state. However, the decreased intensity of the proton resonance signal of the 1-position in **7** (Table 1) suggests that there is equilibrium between the ketonyl and enol forms of the complex in D$_2$O solution. Equilibrium between the π- and σ-type coordination was observed previously in the Pt(III)$_2$−CH$_2$CHO complex in aqueous solution.[24] The increased contribution of the enol form in **7** compared to **3**, **10**, and **12** is probably due to the hydroxyl group bound to the C3 of **7**, which stabilizes the enol form by hydrogen bonding. The distance

Table 2. Selected Bond Distances for $3 \cdot H_2O$, $7 \cdot 0.5C_3H_4O$, **10**, and **12** (Å)

	$3 \cdot H_2O$	$7 \cdot 0.5C_3H_4O$	10	12
Pt1−Pt2	2.6879(9)	2.7002(7)	2.6928(5)	2.7221(16)
Pt1−C1	2.105(18)	2.097(14)	2.088(10)	2.146(13)
C1−C2	1.41(3)	1.50(2)	1.503(17)	1.44(3)
C1−C4				1.60(6)
O1−C2	1.23(3)	1.15(7)	1.221(18)	1.24(3)
C2−C3	1.57(3)	1.60 (2)	1.46(2)	1.45 (4)
O2−C3		1.60(2)	1.40(2)	
C3−C4	1.43(3)			
C4−C5	1.54(4)			

Table 3. Selected Bond Angles and Torsion Angles (deg) for $3 \cdot H_2O$, $7 \cdot 0.5C_3H_4O$, **10**, and **12**

	$3 \cdot H_2O$	$7 \cdot 0.5C_3H_4O$	10	12
	Bond Angles			
C1−Pt1−Pt2	173.5(6)	171.9(5)	169.4(4)	172.4(4)
C2−C1−Pt1	113.7(12)	112(2)	112.9(18)	111.5(11)
O1−C2−C1	126(2)	129(5)	122.0(15)	132(3)
C1−C2−C3	118.6(19)	100(3)	118.9(13)	108(3)
O1−C2−C3	115(2)	131(4)	119.0(14)	119(3)
	Torsion Angles			
Pt1−C1−C2−O1	−94(2)	−69(8)	83.8(16)	66(4)
Pt1−C1−C2−C3	86.7(19)	110(6)	−91.6(13)	100.9(17)
C4−C1−C2−C3				33(4)
O1−C2−C3−O2		−3(12)	172.5(15)	

between O1A and O2A is 2.69 Å, suggesting hydrogen bonding. In the methoxy-substituted complex **10**, such an effect is not observed.

The selected bond lengths and bond angles of complexes $3 \cdot H_2O$, $7 \cdot 0.5C_3H_4O$, **10**, and **12** are listed in Tables 2 and 3.

**Competitive Reaction of 1 with a Mixture of 1-Pentyne and 1-Pentene.** An equimolar mixture of 1-pentyne and 1-pentene was reacted with **1** in D_2O at room temperature to give complexes **3** and $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2(CH_2CH-(OD)CH_2CH_2CH_3)](NO_3)_3$ (**14**), respectively, at a molar ratio of 9:1 on the basis of the ^1H NMR analysis (eq 3). This indicates that alkyne is more reactive than alkene. The result is in accordance with the general tendency that alkynes more easily coordinated to transition metals than alkenes.[29]


(3)

$$\text{The molar ratio} \atop \text{complex 3 : complex 14 = 9 : 1}$$
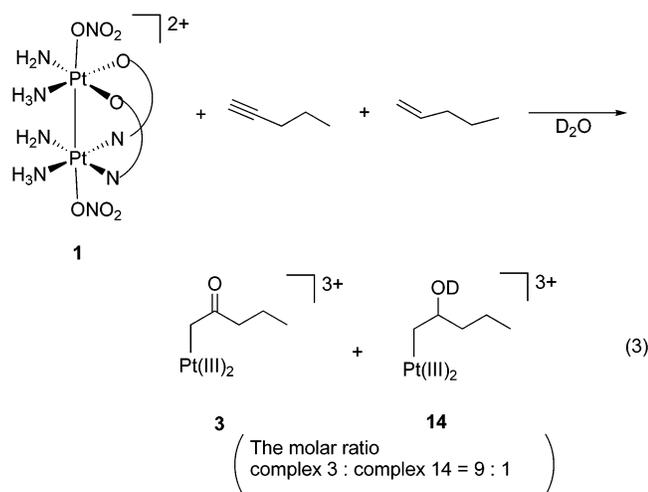
Reactivity of the Ketonyl−Pt(III) Complexes toward Amines. It is known that the alkyl groups in the previous alkyl−platinum(III) complexes undergo nucleophilic attack.[22,23,25] The property is in contrast to the usual alkyl−transition-metal complexes, which react with electrophiles, such as acid and

halogens.[29] By taking advantage of the electrophilic nature of the ketonyl−Pt(III) dinuclear complexes, nucleophile-substituted ketones were synthesized from the reactions of the ketonyl−Pt(III) complexes; reactions with OH^-, halides, and $HNEt_2$ (secondary amines) released α-hydroxyketones, α-halogenoketones, and diethylaminoketones, respectively.[22,23] In the present study, reactions with primary and tertiary amines as well as secondary amines were examined.

Treatment of **3** with propylamine in $CDCl_3$ at room temperature generated the corresponding α-propylaminoketone, as shown in eq 4. After 5 min, formation of the α-aminoketone was confirmed with ^1H NMR and GC/MS spectroscopy of the reaction solution. After 24 h of the reaction, the α-aminoketone totally disappeared and diimine appeared in the ^1H NMR spectrum as eq 4 shows. The latter product was also confirmed with GC/MS spectroscopy. In the ^1H NMR spectrum, 2-pentanone and unidentified products were also observed for the reason mentioned below.

(4)
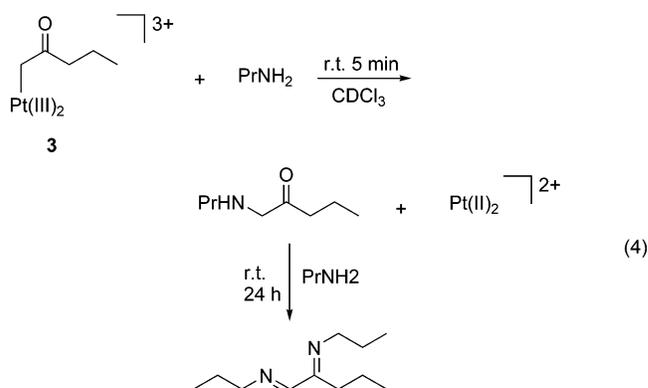
The reaction of **3** with a bulkier primary amine, *tert*-butylamine, was also attempted. In this case α-aminoketone and iminoketone were observed in the ^1H NMR and GC/MS spectra as in eq 5. It seems that bulkier $^tBuNH_2$ does not react with the carbonyl groups of the iminoketone. A less reactive amine, aniline, also reacts with **3**, and only aminoketone is formed as in eq 6. In this case, neither iminoketone nor diimine was obtained.

(5)

(6)
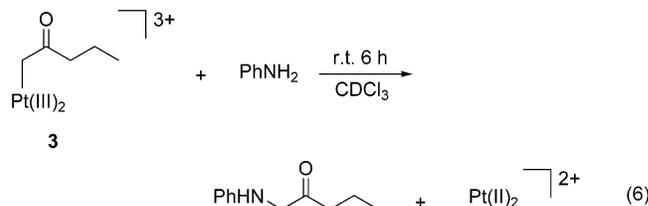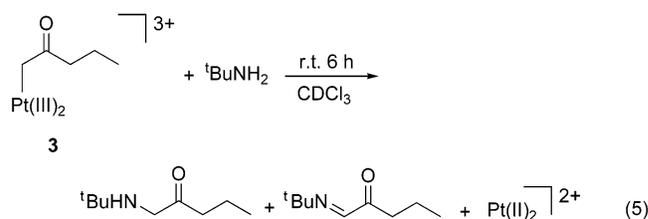
On the basis of the reactions of eqs 4−6, it is concluded that primary amine reacts with **3** to give aminoketone, which is then totally converted to iminoketone and finally to diimine, if the amine is reactive enough and is not sterically bulky. To consider

Scheme 2

$Y = Br$ or $Pt(III)_2$ (**13**)
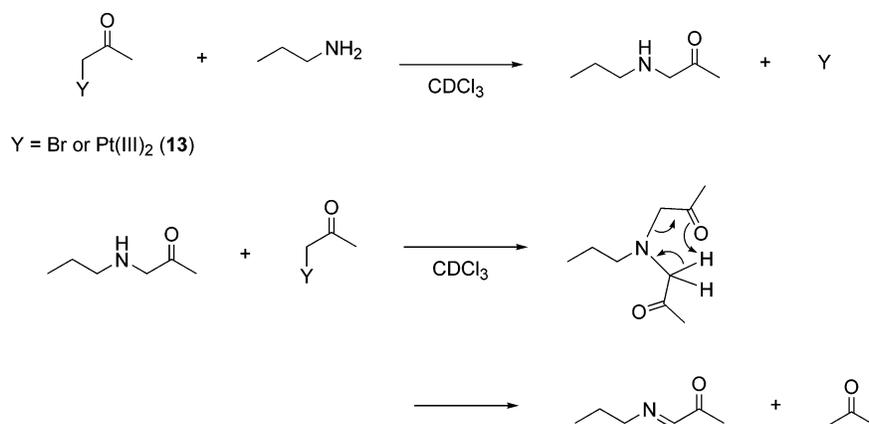
the reaction mechanism, the model reaction was carried out as follows. Bromoacetone having a leaving group in the α-position of the carbonyl group was reacted with excess propylamine in CDCl₃. The reaction was monitored with ¹H NMR spectroscopy, and the same products as for the reaction of **13** with propylamine were obtained (see the Experimental Section). Therefore, the reaction mechanism is proposed as in Scheme 2. The once formed α-aminoketone is still reactive and attacks the excess bromoacetone or **13**, and the resulting diacetonylpropylamine undergoes intramolecular hydrogen transfer and elimination of acetone to form the propyliminoacetone. The succeeding conversion of the iminoketone to diimine is a well-known organic reaction. The released acetone and unidentified products were also observed in the ¹H NMR spectrum. We could not identify and quantify all of these products.

Treatment of the ketonyl complexes **3**–**6** with secondary amine HNEt₂ in CDCl₃ at room temperature generated α-aminoketones Et₂NCH₂CO(CH₂)ₙCH₃ ($n = 2$–5), respectively, in quantitative amount as identified by ¹H NMR and GC/MS spectroscopy (eq 7). In the reactions, the corresponding platinum(II) dinuclear complex was released as a yellow precipitate.

3, R = (CH₂)₂CH₃
4, R = (CH₂)₃CH₃
5, R = (CH₂)₄CH₃
6, R = (CH₂)₅CH₃

(7)
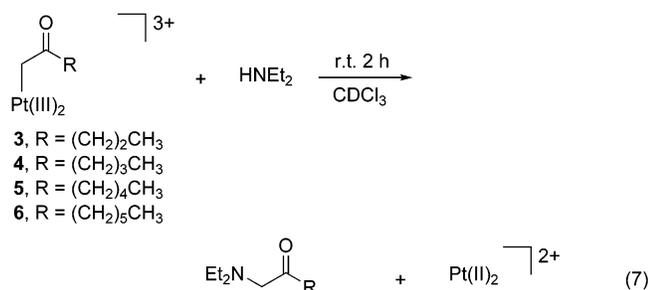
The above reactions give a valuable route to prepare α-aminoketones from alkynes. The reactions proceed almost quantitatively.

The reaction of **3** with less donating *N*-ethylaniline in CDCl₃ gave only α-aminoketone as expressed in eq 8.

(8)
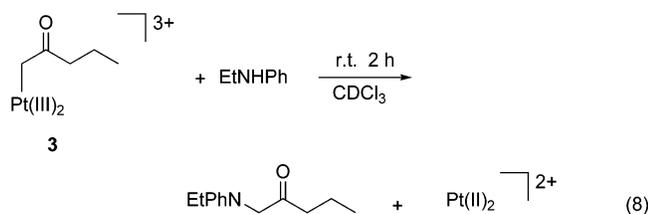
The reaction of **3** with tertiary amine was also attempted, and α-keto quaternary ammonium salt was formed as in eq 9.

(9)
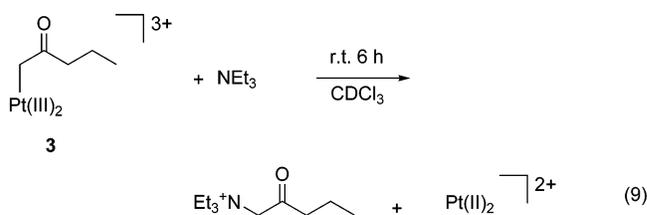
Complex **12** having a secondary carbon atom bound to the Pt(III) atom gave no corresponding aminoketone in the reactions with secondary and tertiary amines. In these cases, unidentified decomposition products were observed in the ¹H NMR spectra. Only 3-buten-2-one was identified in a low yield in the reaction with triethylamine (eq 10). This result indicates that the steric hindrance and the electron-donating nature of the methyl group bound to the α-carbon of the ketonyl ligand prevent the nuclephilic attack of amines. However, primary amine PrNH₂ can react with **12** to give 3-propylamino-2-butanone, 3-propylimino-2-butanone, and 5,6-dimethyl-4,7-diazadecane-4,6-diene as a mixture (eq 11). All these compounds were identified by comparison of the ¹H NMR spectra with those of the authentic samples.[31]

(10)

(11)

Table 4. Reaction of the Ketonyl−Pt(III)$_2$ Complexes with Amines

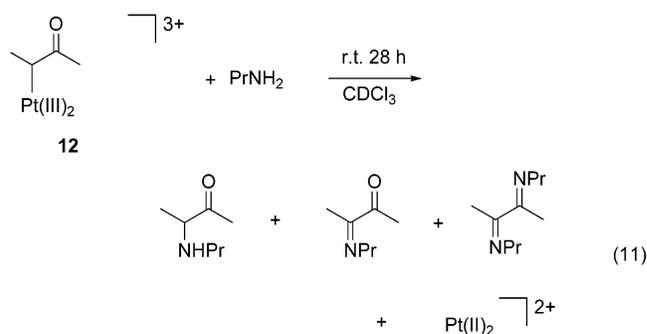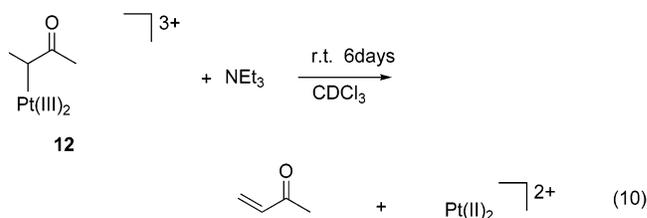| entry	complex	amine	condition	product	yield[1]% (conversion[2]%)
		PRIMARY AMINES			
1	**3**	Pr NH$_3$	r.t. 24 h		45 (90)
2	**13**	Pr NH$_3$	r.t. 24 h		46 (92)
3	**3**	^{t}BuNH$_3$	r.t. 3 days		15
					30 (60)
4	**3**	^{t}BuNH$_3$	40 °C, 2 days		41 (82)
5	**3**	PhNH$_3$	r.t. 6 h		84
6	**12**	∼∼NH$_2$	r.t. 28 h		11(22)
					5 (10)
					8
		SECONDARY AMINES			
7-10	**3-6**	Et$_2$NH	r.t. 6 h	R = (CH$_2$)$_n$CH$_3$, n = 2-5	100 (quantitatively)
11	**3**	Et(Ph)NH	40 °C, 24 h		86
		TERTIARY ANINE			
12	**3**	Et$_3$N	r.t. 6 h		80
13	**12**	Et$_3$N	r.t. 6days		38

[a] Notes: (1) The yield was calculated on the basis of the ^{1}H NMR integrations. Yield = amt of product (mol)/amt of ketonyl−Pt(III) complex used (mol). (2) Conversion = amt of consumed ketonyl−Pt(III) (mol)/amt of ketonyl−Pt(III) complex used (mol).

The reaction of **3** with a less basic nucleophile, sodium acetate, was also attempted in methanol, but no reaction proceeded.

The above reactions are summarized in Table 4, and the following conclusions can be drawn. Primary amines react with complex **3** to form α-aminoketones. This reaction is noteworthy, since primary amines usually react with carbonyl carbon atoms of free ketones in the absence of the Pt(III) complex. The α-aminoketones further undergo dehydrogenation to iminoketones, and diimines are finally produced if the amines are not too bulky. It is known that various ketones easily react with the Pt(III) dinuclear complex **1** to form the corresponding ketonyl−Pt(III) dinuclear complexes.[23] Therefore, the Pt(III) dinuclear complex is a good reaction center to convert either ketones or alkynes to α-aminoketones, iminoketones, and diimines.

The reaction with secondary amines exclusively gives α-aminoketones. It is noteworthy that less basic amines such as aniline and aniline derivatives or even a tertiary amine react with the ketonyl−Pt(III) complex to give α-aminoketones. In all of the reactions above, complex **1** was reduced to the Pt(II)$_2$ dinuclear complex [Pt$_2$(NH$_3$)$_4$((CH$_3$)$_3$CCONH)$_2$]$^{2+}$ and precipitated as yellow powder. To confirm this, the ^{1}H and [195]Pt NMR spectra were measured in D$_2$O. In the ^{1}H NMR spectrum, only a singlet peak was observed at 1.0 ppm which is assigned to the pivalamidate (^{t}Bu) protons of the Pt(II)$_2$ dimer complex. The chemical shift was exactly the same as for the reactions previously reported for the Pt(II)$_2$ dimer complex.[22] The high-field shift compared to the Pt(III) dimer (1.2 ppm) was caused by the shielding effect of the lowered platinum oxidation state.

(31) For preparing authentic compounds see: (a) *Merck Index*, 10th ed.; ONR-92. (b) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555,

The ^{195}Pt NMR spectrum also indicated the Pt(II) dinuclear complex was formed. (see the Experimental Section).

It is clear that the high electron-withdrawing ability of the Pt(III) atom is responsible for the novel reactivity of the ketonyl−Pt(III) complexes toward amines. In this regard, the reactivity should be compared to those of Pt(IV) and Pt(II): several nucleophilic attacks on alkyl−platinum(IV) complexes and other high oxidation state metals such as Rh(III) were reported previously.[32] A detailed mechanistic study of the reductive elimination step of the Pt(IV) complex *fac*-L$_2$PtMe$_3$-(OR) (L = bis(diphenylphosphino)ethane, *o*-bis(diphenylphosphino)benzene, R = acetyl, aryl; L = PMe$_3$, R = aryl) was performed. In the reaction, C−O coupling or C−C coupling products were given depending on the reaction conditions.[32e] Nucleophilic attack of amines on the ketonyl−Pt(III)$_2$ complexes is caused by such a Pt(IV) character, whereas in Pt(II) chemistry, nucleophilic attack is known only to a cationic alkyl−platinum-(II) complex, and all other alkyl−Pt(II) complexes undergo electrophilic attack. A methyl−Hg(II) complex is also known to exhibit an electrophilic property.[33] In these reported reaction systems, however, reaction of ketonyl ligands is not reported. The importance of the present reaction is that Pt(III) reacts with alkynes and the resulting ketonyl−Pt(III) complexes undergo nucleophilic attack.

Conclusions

Treatment of the Pt(III)$_2$ dimer complex **1** with a series of alkynes in aqueous solution leads to formation of the corresponding ketonyl−platinum(III) dinuclear complexes. The process involves initial axial π-coordination of the triple bond to the Pt(III) atom, followed by nucleophilic attack of water. Such alkyne to ketonyl transformation shows the strong electron-withdrawing effect of Pt(III). Interestingly, the ketonyl−platinum(III) compounds react with amines to give various α-amino-substituted ketones. Primary, secondary, and tertiary amines react with the ketonyl−platinum(III) complexes. In the reaction with primary amines, the resulting α-aminoketones further undergo conversion to α-iminoketones and diimines. Although quite a number of ketonyl−transition-metal compounds are known, ketonyl ligands usually do not show reactions, and their reactivity is limited. The present reactions are almost the first to release conversion products.

It should be emphasized here that, without the Pt(III)$_2$ complex, ketones react with amines at the carbonyl carbon to give Schiff bases. Considering the easy ketonyl−Pt(III)$_2$ complex formation from ketones,[23] the present reaction provides a unique method for α-nucleophile modification of ketones.

Experimental Section

Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II elemental analyzer. The ^{1}H NMR spectra were recorded on a JEOL EX-270 spectrometer operating at 270 MHz for ^{1}H and on a JEOL Lambda 500 spectrometer operating at 107.3 MHz for ^{195}Pt. Chemical shifts are reported in δ units (parts per million, ppm) referenced to Me$_4$Si at 0 ppm (CDCl$_3$) or to Me$_4$NClO$_4$ at 3.19

ppm (D$_2$O) for ^{1}H and to Na$_2$PtCl$_6$ (external reference, 0 ppm) and K$_2$PtCl$_4$ (external reference, −1624 ppm) for ^{195}Pt. The mass spectra were measured on a JEOL AUTOMASS spectrometer and JEOL SX-102A spectrometer. The IR spectra were recorded on a HITACHI I-3000 spectrometer. Alkynes, solvents, and amines were commercially available ones. The platinum blue complex **2**[24] was synthesized as reported in the literature.

Reaction of 1 with Alkynes. General Procedure. In a typical experiment, to a solution of **2** (0.050 g, 0.0307 mmol) in water (1 mL) was added Na$_2$S$_2$O$_8$ (0.015 g, 0.0615 mmol) at room temperature. After the dark blue solution completely changed to yellow, 1-pentyne (0.030 mL, 0.307 mmol) was added, and the mixture was stirred for 1 h at room temperature. The reaction mixture was kept at 5 °C for 1 day to give yellow precipitate, which was filtered, washed with cold water, and dried to obtain a yellow powder of **3** (yield, 67%). Anal. Calcd for C$_{15}$H$_{41}$N$_9$O$_{12}$Pt$_2$: C, 19.38; H, 4.45; N, 13.56. Found: C, 19.38; H, 4.27; N, 13.12. IR: $\nu_{C=O}$ = 1596 cm^{-1}.

The same procedure as for the reaction with 1-pentyne forming **3** was employed for the reactions with 1-hexyne, 1-heptyne, 1-octyne, 2-propyn-1-ol, 3-butyn-1-ol, 4-pentyn-1-ol, methyl propargyl ether, phenylacetylene, and 2-butyne, giving complexes **4**−**12**, respectively. The ^{1}H NMR spectra of complexes **11** and **12** were the same as those of the reaction products of complex **2** with acetophenone and butanone, respectively, in the presence of concentrated HNO$_3$,[23] showing the same products are obtained. The yields and elemental analyses are as follows. (**4**) Yield: 65%. Anal. Calcd for C$_{16}$H$_{43}$N$_9$O$_{12}$Pt$_2$: C, 20.36; H, 4.59; N, 13.36. Found: C, 19.97; H, 4.62; N, 13.11. IR: $\nu_{C=O}$ = 1599 cm^{-1}. (**5**) Yield: 70%. Anal. Calcd for C$_{17}$H$_{45}$N$_9$O$_{12}$Pt$_2$: C, 21.32; H, 4.74; N, 13.16. Found: C, 20.96; H, 4.58; N, 12.89. IR: $\nu_{C=O}$ = 1599 cm^{-1}. (**6**) Yield: 45%. Anal. Calcd for C$_{18}$H$_{47}$N$_9$O$_{12}$Pt$_2$: C, 22.25; H, 4.87; N, 12.97. Found: C, 22.44; H, 4.65; N, 12.99. IR: $\nu_{C=O}$ = 1598 cm^{-1}. (**7**·0.5C$_3$H$_4$O) Yield: 55%. Anal. Calcd for C$_{14.5}$H$_{39}$N$_9$O$_{13.5}$Pt$_2$: C, 18.42; H, 4.16; N, 13.33. Found: C, 18.46; H, 4.02; N, 13.08. IR: $\nu_{C=O}$ = 1585 cm^{-1}. (**8**) Yield: 67%. Anal. Calcd for C$_{14}$H$_{39}$N$_9$O$_{13}$Pt$_2$: C, 18.05; H, 4.22; N, 13.53. Found: C, 18.37; H, 3.88; N, 13.24. IR: $\nu_{C=O}$ = 1594 cm^{-1}. (**9**) Yield: 88%. Anal. Calcd for C$_{15}$H$_{41}$N$_9$O$_{13}$Pt$_2$: C, 19.05; H, 4.37; N, 13.33. Found: C, 18.97; H, 4.37; N, 12.98. IR: $\nu_{C=O}$ = 1632 cm^{-1}. (**10**) Yield: 55%. Anal. Calcd for C$_{14}$H$_{39}$N$_9$O$_{13}$Pt$_2$: C, 18.05; H, 4.22; N, 13.53. Found: C, 17.82; H, 4.05; N, 13.16. IR: $\nu_{C=O}$ = 1597 cm^{-1}. (**11**) Yield: 70%. Anal. Calcd for C$_{18}$H$_{39}$N$_9$O$_{12}$Pt$_2$: C, 22.43; H, 4.08; N, 13.08. Found: C, 22.14; H, 3.95; N, 12.53. IR: $\nu_{C=O}$ = 1597 cm^{-1}. (**12**) Yield: 69%. Anal. Calcd for C$_{14}$H$_{39}$N$_9$O$_{12}$Pt$_2$: C, 18.36; H, 4.29; N, 13.77. Found: C, 18.16; H, 4.20; N, 13.46. IR: $\nu_{C=O}$ = 1600 cm^{-1}.

Method for the Preparation of the Crystals of 3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10, and 12. To complex **2** (0.010 g, 0.00615 mmol) in H$_2$O (0.5 mL) was added Na$_2$S$_2$O$_8$ (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$_3$ (0.050 mL) and 1-pentyne (0.020 mL) to the yellow solution and letting the mixture stand for a few days at room temperature gave yellow crystals of **3·H$_2$O. Using 2-propyn-1-ol, 4-pentyn-1-ol, methyl propargyl ether, and 2-butyne instead of 1-pentyne afforded yellow crystals of **7·0.5C$_3$H$_4$O, 9, 10**, and **12**, which were used for the X-ray diffraction analysis.

Competitive Reaction of 1-Pentyne and 1-Pentene with Complex 1. To a solution of complex **1** (0.016 g, 0.01 mmol) in D$_2$O (0.6 mL) was added Na$_2$S$_2$O$_8$ (0.005 g, 0.02 mmol). After the dark blue solution was converted to yellow, the solution was transferred to an NMR tube, and 1-pentyne (0.01 mL, 0.1 mmol) and 1-pentene (0.011 mL, 0.1 mmol) were added. After 1 h at room temperature, the reaction mixture was analyzed with ^{1}H NMR spectroscopy, which indicates the formation of complexes **3** and **14** at a molar ratio of 9:1. ^{1}H NMR (D$_2$O, δ, 270 MHz, 293 K) for **14**: 4.51 (dd, 1H, $^2J_{PtH}$ = 38 Hz, $^2J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 3.0 Hz, PtCH$_2$), 4.01 (t, 1H, $^2J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz PtCH$_2$), 3.72 (m, 1H, CH$_2$C*H*(OH)CH$_2$), 1.79 (q, 2H, $^3J_{HH}$ = 7.6 Hz, CH$_2$C*H$_2$*-

(32) (a) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004. (b) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385. (c) Romero, P.; Valderrama, M.; Contreras, R.; Boys, D. *J. Organomet. Chem.* **2003**, *673*, 102. (d) Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* **1979**, *179* (4), C61. (e) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576.
(33) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Jwentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340.

Table 5. Summary of the Crystal Data for Complexes **3**·H_2O, **7**·$0.5C_3H_4O$, **10**, and **12**

	3·H_2O	7·$0.5C_3H_4O$	10	12
empirical formula	$C_{15}H_{43}N_9O_{13}Pt_2$	$C_{14.5}H_{39}N_9O_{13.5}Pt_2$	$C_{14}H_{39}N_9O_{13}Pt_2$	$C_{14}H_{39}N_9O_{12}Pt_2$
fw	947.76	949.76	931.72	915.72
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$P2_1/c$ (No.2)	$P\bar{1}$ (No.2)
a (Å)	9.6251(17)	9.6133(6)	9.4625(4)	9.807(8)
b (Å)	10.1925(18)	10.0893(7)	10.0973(4)	10.045(8)
c (Å)	15.986(3)	17.1561(11)	30.1278(12)	14.742(11)
α (deg)	84.335(3)	106.867(1)	90	88.363(14)
β (deg)	78.348(4)	100.741(1)	96.449(1)	82.960(14)
γ (deg)	89.358(3)	93.340(1)	90	84.854(14)
V (Å^3)	1528.4(5)	1533.3(2)	2860.4(2)	1433.5(19)
T (K)	223 ± 1	298 ± 1	293 ± 2	293 ± 2
Z	2	2	4	2
ρ_{calcd} (gcm^{-3})	2.024	1.932	2.164	2.122
cryst dimens (mm)	0.5 × 0.3 × 0.1	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.09	0.5 × 0.3 × 0.1
abs coeff (cm^{-1})	92.11	90.57	98.14	98.16
2θ range (deg)	4 < 2θ < 55	2.5 < 2θ < 46	2.7 < 2θ < 62	2.8 < 2θ < 47
no. of obsd unique reflns	3198 ($I > 2\sigma(I)$)	4412 ($I > 2\sigma(I)$)	8349 ($I > 2\sigma(I)$)	4060 ($I > 2\sigma(I)$)
no. of params	360	357	328	347
R^a	0.075	0.046	0.056	0.036
$R_w{}^b$	0.190	0.124	0.143	0.093
GOF^c	0.990	0.942	1.097	1.057

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

CH_2), 1.49 (quin, 2H, $^3J_{HH}$ = 7.6 Hz, CH$_2$C*H$_2$*CH$_3$), 1.19 (s, 18H, 2*Me$_3$*-CCONH), 0.96 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH$_2$C*H$_3$*).

Reactions of Ketonyl−Platinum(III) Dinuclear Complexes with Amines. The reactions of the 1-pentanonyl complex **3** with primary, secondary, and tertiary amines were examined as follows. In a typical experiment, to a suspension of 1-pentanonyl−diplatinum(III) complex **3** (0.018 g, 0.02 mmol) in CDCl$_3$ (0.6 mL) was added PrNH$_2$ (0.10 mmol) at room temperature. After the mixture was stirred for 5 min, the yellow precipitate of the reduced diplatinum(II) complex [Pt(II)$_2$-(NH$_3$)$_4$((CH$_3$)$_3$CCONH)$_2$]$^{2+}$ was filtered off, and the pale yellow filtrate was analyzed with ^{1}H NMR and GC/MS spectroscopy. Both of the spectra identified PrNHCH$_2$CO(CH$_2$)$_2$CH$_3$ in the solution as the exclusive product. The yellow precipitate was confirmed to be the Pt(II) dinuclear complex [Pt(II)$_2$(NH$_3$)$_4$((CH$_3$)$_3$CCONH)$_2$]$^{2+}$ with ^{195}Pt NMR spectroscopy in D$_2$O. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.49 (s, 2H, H^1), 2.53 (t, $^3J_{HH}$ = 7.1 Hz, 2H, NHC*H$_2$*C$_2$H$_5$), 2.37 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H^3), 1.63 (m, 2H, H^4), 1.52 (m, 2H, NHCH$_2$C*H$_2$*CH$_3$), 0.93 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NHC$_2$H$_4$C*H$_3$*), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, H^5). MS (EI) m/z (relative intensity): 112 (M$^+$ − Et − 2H, 16), 99 (4), 84 (33), 70 (100). ^{195}Pt{^{1}H} NMR of the Pt(II) dinuclear complex (D$_2$O, δ, 107.3 MHz): −1425 (H−H, N$_2$O$_2$-coordinated), −2376 (H−H, N$_4$-coordinated), and −1923 (H−T, N$_3$O-coordinated). The assignment of these peaks was done by comparison with the reported data of the Pt(II) dinuclear complexes having analogous bridging ligands^3 and with that of the in situ generated pivalamide-bridged Pt(II) dinuclear complex.^{34} The fast HH−HT isomerization was also reported in the acetamidate-bridged platinum(II) dinuclear complex.^{35}

The above solution was further reacted for 24 h, and by using CHCl$_2$-CHCl$_2$ as the internal reference, the ^{1}H NMR and GC/MS spectra were measured in CDCl$_3$ after the excess PrNH$_2$ was expelled with N$_2$ stream. Both of the spectra showed that the original peaks of PrNHCH$_2$CO-(CH$_2$)$_2$CH$_3$ totally disappeared and new peaks ascribed to PrN=CC-(=NPr)Pr appeared. Yield: 45% (conversion of **3**, 90%). ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 7.74 (s, 1H, H^1), 3.51 (t, $^3J_{HH}$ = 7.5 Hz, 2H, NC*H$_2$*C$_2$H$_5$), 3.48 (t, J = 7.1 Hz, 2H, NC*H$_2$*C$_2$H$_5$), 2.56 (t, J = 7.6 Hz 2H, H^3), 1.73 (m, 2H, NCH$_2$C*H$_2$*CH$_3$), 1.68 (m, 2H, NCH$_2$C*H$_2$*CH$_3$), 1.61 (m, 2H, H^4), 0.98 (t, J = 7.4 Hz, 3H, NC$_2$H$_4$C*H$_3$*), 0.96 (t, J =

7.4 Hz, 3H, NC$_2$H$_4$C*H$_3$*), 0.91 (t, J = 7.3 Hz, 3H, H^5). MS (EI) m/z (relative intensity): 182 (M$^+$, 2), 153 (M$^+$ − Et, 91), 111 (21), 96 (9), 84 (52), 70 (100). A similar reaction was attempted with the acetonyl−Pt(III) dinuclear complex **13** (0.015 g) and 5 equiv of PrNH$_2$. The reaction was followed with ^{1}H NMR and GC/MS spectroscopy, and the formation of PrNHCH$_2$COCH$_3$ and PrN=CC(=NPr)CH$_3$ was confirmed. The assignment of the peaks for the latter diimine compound was done by comparison with the authentic compound prepared from pilvinaldehyde (OHCCOCH$_3$) and PrNH$_2$. The GC/MS spectrum of PrN=CC(=NPr)CH$_3$ shows that the largest peak is not the mother peak, but the M$^+$ − Et peak, and it seems that the mother ion easily loses the Et group in GC/MS. ^{1}H NMR (CDCl$_3$, δ, 270 MHz) for 1-propylamino-2-propanone: 3.53 (s, 2H, NHC*H$_2$*CO), 2.54 (t, $^3J_{HH}$ = 7.2 Hz, 2H, NHC*H$_2$*C$_2$H$_5$), 2.14 (s, 3H, COC*H$_3$*), 1.50 (q, 2H, NHCH$_2$C*H$_2$*CH$_3$), 0.92 (t, 3H, NHC$_2$H$_4$C*H$_3$*). MS (EI) for 1-propyl-amino-2-propanone, m/z (relative intensity): 115 (M$^+$, 14), 100 (4), 86 (46), 73 (100), 57 (62). Yield for 5-methyl-4,7-diazadecane-4,6-diene: 46% (conversion of **13**, 92%). ^{1}H NMR (CDCl$_3$, δ, 270 MHz) for 5-methyl-4,7-diazadecane-4,6-diene: 7.81 (s, 1H, N=C*H*C=N), 3.52 (t, $^3J_{HH}$ = 7.0 Hz, 2H, NC*H$_2$*C$_2$H$_5$), 3.43 (t, $^3J_{HH}$ = 7.0 Hz, 2H, NC*H$_2$*C$_2$H$_5$), 2.17 (s, 3H, COC*H$_3$*), 1.71 (m, 4H, NCH$_2$C*H$_2$*CH$_3$), 1.05 (m, 6H, NC$_2$H$_4$C*H$_3$*). MS (EI) for 5-methyl-4,7-diazadecane-4,6-diene, m/z (relative intensity): 154 (M$^+$, 3), 125 (M$^+$ − Et, 100), 96 (63), 83 (41), 69 (23), 56 (21).

For comparison, a bulkier primary amine, *tert*-butylamine, was used for the reaction with **3**. To a suspension of **3** (0.015 g) in CDCl$_3$ (0.6 mL) was added *tert*-butylamine (5 equiv), and the solution was reacted for 6 h at room temperature. The solution gave a yellow precipitate of the pivalamide-bridged Pt(II) dinuclear complex, which was filtered off, and the solution was analyzed with ^{1}H NMR spectroscopy. Different from propylamine, bulky *tert*-butylamine did not react immediately; however, after 3 days of the reaction, aminoketone ^{t}BuNHCH$_2$CO-(CH$_2$)$_2$CH$_3$ and iminoketone ^{t}BuN=CHCO(CH$_2$)$_2$CH$_3$ were gradually produced. Yield for 1-*tert*-butylamino-2-pentanone: 15%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz) for 1-*tert*-butylamino-2-pentanone: 4.24 (s, 2H, H^1), 2.41 (t, J = 7.3 Hz, 2H, H^3), 1.61 (m, 2H, H^4), 0.92 (t, J = 7.3 Hz, 3H, H^5). MS (EI) for 1-*tert*-butylamino-2-pentanone, m/z (relative intensity): 157 (M$^+$, 4), 127 (79), 113 (34), 86 (80). Yield for 1-*tert*-butylimino-2-pentanone: 30% (conversion of **3**, 60%). ^{1}H NMR (CDCl$_3$, δ, 270 MHz) for 1-*tert*-butylimino-2-pentanone: 7.56 (s, 1H, H^1), 2.82 (t, J = 7.3 Hz, 2H, H^3), 1.64 (m, 2H, H^4), 0.95 (t, J = 7.3 Hz, 3H, H^5). MS (EI) for 1-*tert*-butylimino-2-pentanone, m/z (relative

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intensity): 155 (M$^+$, 10), 140 (100), 127 (79), 113 (34), 84 (72). Reaction of more than 3 days resulted in the decomposition of the complex. A slightly better yield of 1-*tert*-butylimino-2-pentanone was realized by performing the reaction at 40 °C for 2 days (Table 4, entry 4).

The reaction of **3** with aniline was carried out for 6 h, similar to other amines described above, and the ^{1}H NMR spectrum of the filtrate showed that only aminoketone was formed. Yield: 84%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.97 (s, 2H, H^1), 2.48 (t, J = 7.2 Hz, 2H, H^3), 1.69 (m, 2H, H^4), 0.95 (t, J = 7.3 Hz, 3H, H^5). MS (EI) m/z (relative intensity): 177 (M$^+$, 4), 106 (M$^+$ − COC$_3$H$_7$, 100), 77 (15).

The reaction of complex **12** having a secondary carbon atom bound to the Pt(III) atom with propylamine was carried out as follows. To a suspension of **12** (0.009 g) in CDCl$_3$ (1.0 mL) was added propylamine (5 equiv), and the solution was monitored with ^{1}H NMR spectroscopy for 7 days at room temperature. After the mixture was stirred for 6 h, 3-propylamino-2-butanone appeared. At the same time, 3-propylimino-2-butanone and 5,6-dimethyl-4,7-diaza-4,6-decadiene were gradually formed. After 28 h, these compounds were observed as a mixture in low yields. The three products were identified by comparison with the ^{1}H NMR spectra of the authentic compounds. Yield of 3-propylamino-2-butanone: 8%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz) of 3-propylamino-2-butanone:[31a] 3.30 (q, 1H, 7.2 Hz, CH$_3$C*H*(NHPr)CO), 2.42 (t, 2H, 7.0 Hz, NHC*H*$_2$CH$_2$), 2.13 (s, 3H, COC*H*$_3$), 1.45 (m, 2H, CH$_2$C*H$_2$*-CH$_3$), 1.19 (d, 3H, 7.2 Hz, CHC*H*$_3$), 0.86 (t, 7.6 Hz, CH$_2$C*H*$_3$). Yield of 3-propylimino-2-butanone: 5% (conversion of **12**, 10%). ^{1}H NMR (CDCl$_3$, δ, 270 MHz) of 3-propylimino-2-butanone:[31b] 3.39 (t, 2H, 6.8 Hz, NC*H*$_2$CH$_2$), 2.35 (s, 3H, COC*H*$_3$), 1.90 (s, 3H, NCC*H*$_3$), 1.69 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 0.96 (t, 3H, 7.0 Hz, CH$_2$C*H*$_3$). Yield of 5,6-dimethyl-4,7-diaza-4,6-decadiene: 11% (conversion of **12**, 22%). ^{1}H NMR (CDCl$_3$, δ, 270 MHz) of 5,6-dimethyl-4,7-diaza-4,6-decadiene:[31b] 3.36 (t, 4H, 7.0 Hz, 2(NC*H*$_2$CH$_2$)), 2.03 (s, 6H, 2(NC*H*$_3$)), 1.68 (m, 4H,2-(CH$_2$C*H*$_2$CH$_3$)), 0.96 (t, 6H, 2(CH$_2$CH$_2$C*H*$_3$)). Unidentified decomposition products gradually appeared for more than 2 days of the reaction.

The reaction of secondary amines was carried out as follows. To a suspension of pentanonyl−Pt(III) dinuclear complex **3** (0.018 g, 0.02 mmol) in CDCl$_3$ (0.6 mL) was added HNEt$_2$ (0.041 mL, 0.40 mmol) at room temperature. After the mixture was stirred for 2 h, a yellow precipitate was formed, which was filtered. The pale yellow filtrate was analyzed with ^{1}H NMR and GC/MS spectroscopy to confirm Et$_2$-NCH$_2$CO(CH$_2$)$_2$CH$_3$ as the exclusive conversion product. By using CHCl$_2$CHCl$_2$ as the internal reference, the quantitative conversion was confirmed by the ^{1}H NMR spectrum. The yellow precipitate was confirmed to be the Pt(II) dimeric complex with ^{195}Pt NMR spectroscopy in D$_2$O. ^{1}H NMR (CDCl$_3$, δ, 270 MHz) for 1-diethylamino-2-pentanone: 3.14 (s, 2H, H^1), 2.47 (q, J = 6.8 Hz, 4H, N(C*H$_2$*CH$_3$)$_2$), 2.38 (t, J = 7.5 Hz, 2H, H^3), 1.53 (m, J = 7.1 Hz, 2H, H^4), 0.96 (t, J = 6.8 Hz, 6H, N(CH$_2$C*H$_3$*)$_2$), 0.85 (t, J = 7.2 Hz, 3H, H^5). MS (EI) for 1-diethylamino-2-pentanone, m/z (relative intensity): 157 (M$^+$, 4), 142 (4), 114 (3), 86 (100), 59 (83).

The same procedure as above was used for the reactions of complexes **4**−**6** with HNEt$_2$. The ^{1}H NMR data and the corresponding MS spectra for the amino-substituted ketones are given in the following.

The reaction with complex **4** gave 1-diethylamino-2-hexanone, which was confirmed with ^{1}H NMR and GC/MS spectra. Yield: 100%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.16 (s, 2H, H^1), 2.50 (q, J = 7.0 Hz, 4H, N(C*H$_2$*CH$_3$)$_2$), 2.53 (t, J = 7.4 Hz, 2H, H^3), 1.51 (m, 2H, H^4), 1.26 (m, 2H, H^5), 0.98 (t, J = 7.0 Hz, 6H, N(CH$_2$C*H$_3$*)$_2$), 0.86 (t, J = 7.3 Hz, 3H, H^6). MS (EI) m/z (relative intensity): 171 (M$^+$, 16), 156 (19), 142 (6), 126 (12), 114 (23), 100 (14), 87 (100), 59 (98).

The reaction with complex **5** gave 1-diethylamino-2-heptanone, which was confirmed with ^{1}H NMR and GC/MS spectra. Yield: 100%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.14 (s, 2H, H^1), 2.49 (q, J = 7.2 Hz, 4H, N(C*H$_2$*CH$_3$)$_2$), 2.39 (t, J = 7.5 Hz, 2H, H^3), 1.51 (m, 2H, H^4), 1.3−1.1 (m, 4H, H^5 and H^6), 0.99 (t, J = 7.2 Hz, 6H, N(CH$_2$C*H$_3$*)$_2$), 0.82 (t, J = 7.0 Hz, 3H, H^7). MS (EI) m/z (relative intensity): 185 (M$^+$, 3), 170 (5), 112 (4), 87 (100), 58 (96).

The reaction with complex **6** gave 1-diethylamino-2-octanone, which was confirmed with ^{1}H NMR and GC/MS spectra. Yield: 100%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.13 (s, 2H, H^1), 2.47 (q, J = 7.2 Hz, 4H, N(C*H$_2$*CH$_3$)$_2$), 2.39 (t, J = 7.1 Hz, 2H, H^3), 1.49 (m, 2H, H^4), 1.3−1.0 (m, 6H, H^5 and H^6, and H^7), 0.96 (t, J = 7.2 Hz, 6H, N(CH$_2$C*H$_3$*)$_2$), 0.81 (t, J = 6.9 Hz, 3H, H^8). MS (EI) m/z (relative intensity): 199 (M$^+$, 47), 198 (53), 184 (85), 170 (10), 156 (19), 142 (14), 128 (13), 114 (71), 102 (68), 91 (100), 73 (80), 59 (98).

The reaction of **3** with *N*-ethylaniline was performed at 40 °C for 24 h as described above to give the corresponding aminoketone Ph-(Et)NCH$_2$CO(CH$_2$)$_2$CH$_3$ Yield: 86%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 3.95 (s, 2H, H^1), 3.46 (q, J = 7.2 Hz, 2H, NC*H$_2$*CH$_3$), 2.43 (t, J = 7.3 Hz, 2H, H^3), 1.61 (q, J = 7.4 Hz, 2H, H^4), 1.20 (t, J = 7.2 Hz, 3H, NCH$_2$C*H$_3$*), 0.90 (t, J = 7.4 Hz, 3H, H^5). MS (EI) m/z (relative intensity): 205 (M$^+$, 7), 198 (M$^+$ − COC$_3$H$_7$, 100), 106 (21), 77 (12).

The reaction of **3** with triethylamine was carried out for 6 h to give the corresponding α-keto quaternary ammonium ion Et$_3$N$^+$CH$_2$CO-(CH$_2$)$_2$CH$_3$. Yield: 80%. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 4.83 (s, 2H, H^1), 3.62 (q, J = 7.6 Hz, 6H, N(C*H$_2$*CH$_3$)$_3$), 2.63 (t, J = 7.5 Hz, 2H, H^3), 1.63 (q, J = 7.5 Hz, 2H, H^4), 1.35 (t, J = 7.6 Hz, 9H, N(CH$_2$C*H$_3$*)$_3$), 0.93 (t, J = 7.3 Hz, 3H, H^5). MS (FAB) m/z (relative intensity): 186 (M$^+$).

The reaction of **12** with triethylamine was carried out for 6 days to give 3-buten-2-one in 38% yield. ^{1}H NMR (CDCl$_3$, δ, 270 MHz): 6.32 (dd, J = 18.0 Hz, 10.0 Hz 1H, CH$_2$=C*H*COCH$_3$), 6.17 (d, J = 18.0 Hz, 1H, CH*H*=CHCOCH$_3$), 5.90 (d, J = 10.0 Hz, 1H, C*H*H=CHCOCH$_3$), 2.27 (s, 3H, CH$_2$=CHCOC*H$_3$*).

Crystal Structure Determination of 3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10, and 12. Yellow crystals of **3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10,** and **12** suitable for X-ray diffraction analysis were coated with epoxy resin. Diffraction data of complexes **3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10,** and **12** were collected on a Bruker SMART 1000 CCD diffractometer by using Mo Kα radiation. All the intensity data were processed by a SAINT plus program package. The structure solution was performed with the SHELXTL software package. All non-hydrogen atoms in **3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10,** and **12** were refined anisotropically. For **7·0.5C$_3$H$_4$O,** the elemental analysis, ^{1}H NMR spectrum, and unit cell volume (39 non-hydrogen atoms in the asymmetric unit in V = 1553.30(18) Å^3 and Z = 2) showed that 0.5 molecule of 2-propyn-1-ol (C$_3$H$_4$O) is also contained in the crystal lattice; however, the quality of the collected diffraction data did not allow the atoms to be located and refined. Therefore, the structure analysis was carried out without the 0.5 molecule of C$_3$H$_4$O. Further details of the crystallographic analysis of **3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10,** and **12** are summarized in Table 5 and the Supporting Information.

Supporting Information Available: Full tables of the data collection parameters, isotropic and anisotropic temperature factors, and bond distances and angles for **3·H$_2$O, 7·0.5C$_3$H$_4$O, 9, 10,** and **12**. Crystallographic information is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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