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Reactions of α,*β*-Unsaturated Thioesters with Platinum(0): Implication of a Dual Mechanism Leading to the Formation of Acyl Platinum[†]

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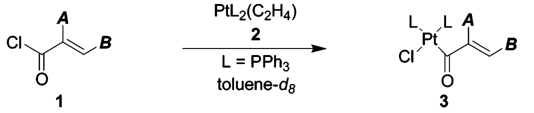
The moderate reactivity of the α,*β*-unsaturated thioester (ArS)C(O)C(***A***)═C(***B***)(H) toward $Pt(PPh_3)_2(C_2H_4)$ has been used to extract thermodynamic and kinetic information pertaining to the oxidative addition of α,*β*-unsaturated acid halide derivatives to low-valent transition-metal complexes. The results indicate acyl platinum product complexes can form by direct C−S bond cleavage or by attack of coordinated $Pt(PPh_3)_2$ on the *β*-carbon.

Introduction

It has been well-known that the reactions of α,*β*-unsaturated acid halides with low-valent transition-metal complexes produced acyl metals.[1] However, much attention to their reaction mechanism has not been attracted presumably due to the lack of a good reaction system to examine the details. In fact, when the reactions of (Cl)C(O)C(H)═CH_2 (***A*** = ***B*** = H; **1a**) or (Cl)C(O)C(H)═C(Ph)(H)-(*E*) (***A*** = H, ***B*** = Ph; **1b**) with $Pt(PPh_3)_2(C_2H_4)$ (**2**) were performed in toluene-d_8 using a freeze−pump−thaw technique, acyl platinums **3a** and **3b** were quantitatively produced even at −50 °C after 10 min in both cases (eq 1).[2] Although the predominant formation of the *cis* isomer at the beginning of the reactions suggested its stereochemistry of oxidative addition, more information such as the effect of the introduction of a Ph group at the *β*-carbon (***B*** = Ph) was not clearly disclosed from these experimental data.



(1)

A = H, ***B*** = H ; **1a**	- 50 °C,10 min	**3a** 100%	(*cis/trans* = 57/43)
	10 °C,10 min	100%	(*cis/trans* = 0/100)
A = H, ***B*** = Ph; **1b**	- 50 °C,10 min	**3b** 100%	(*cis/trans* = 96/4)
	10 °C,10 min	100%	(*cis/trans* = 0/100)

Recently, we have reported that the cleavage and formation of C−S bonds by transition-metal complexes were flexible[3] and that such characteristics could be utilized for elucidating the mechanism of cleavage of the vinyl−X bonds by low-valent transition-metals[4] and for achieving a series of Pt-catalyzed carbothiolation of alkynes.[5] Herein we wish to report that the effects of substituents on the reactions of α,*β*-unsaturated acid halide derivatives with low-valent transition-metal complexes are quite clearly revealed by utilizing the controllable reactivity of the α,*β*-unsaturated thioester (ArS)C(O)C(***A***)═C(***B***)(H) (**4**) toward **2**, substantiating that there are two distinct reaction routes for the formation of acyl complexes.

Results and Discussion

Reactions of Thioesters Having a *p*-MeC_6H_4S Group with a Platinum(0) Complex. Thioesters **4** with a *p*-MeC_6H_4S group shown in Table 1 were prepared, and the reactions with **2** were monitored by ^1H and ^{31}P NMR spectroscopies at 25 °C using S═$P(C_6H_4OMe$-$p)_3$ as an internal standard.[6] When **4a** (***A*** = ***B*** = H) was employed, the quantitative formation of π-complex **5a** was confirmed after 20 min in both C_6D_6 and CD_2Cl_2 solution. Although it was not clear when the systems reached the equilibrium states due to the low yields of acyl platinum **6a** and **7a** (dimeric form of **6a**), the formation after 3 h of 99.5% of **5a** and 0.5% of **7a** in C_6D_6 and of 98.9% of **5a**, 0.4% of **6a**, and 0.7% of **7a** was confirmed in CD_2Cl_2 (runs 1 and 2). On the other hand, the reaction of *trans*-**3a** (0.02 mmol) with *p*-MeC_6H_4SNa (**8**, 0.06 mmol) in CD_2Cl_2 (0.5 mL) at 25 °C produced **5a** (79%), *trans*-**6a** (0.6%), and **7a** (13%, *syn*/*anti* = 77/23) after 17 h (eq 2). These results clearly showed that the

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[†] This work is dedicated to Prof. Hideo Kurosawa on the occasion of his retirement from Osaka University.

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(6) No interaction between S═$P(C_6H_4OMe$-$p)_3$ and other reagents has been confirmed during the course of the present study.

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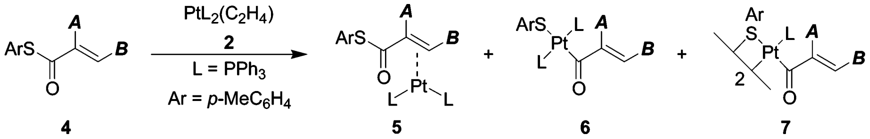
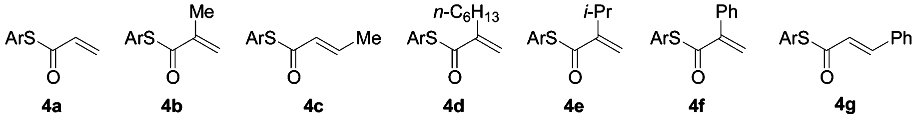
Table 1. Reactions of 4 with 2[a]





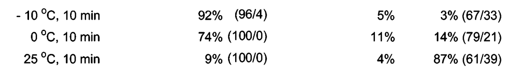
run	4	solvent[b]	time[c]	5/6(*cis*/*trans*)[d]	time[e]	6(*cis*/*trans*)/7(*syn*/*anti*)[d]
1	**4a**	*a*	—[f]	—[g]	—[f]	—[g]
2	**4a**	*b*	—[f]	—[h]	—[f]	—[h]
3	**4b**	*a*	3−4 h	51/49(6/94)	3−4 h	13(6/94)/87(79/21)
4	**4b**	*b*	5−6 h	22/78(13/87)	5−6 h	22(13/87)/78(83/17)
5	**4c**	*a*	<40 min	57/43(0/100)	<40 min	7(0/100)/93(64/36)
6	**4c**	*b*	<40 min	17/83(0/100)	<40 min	20(0/100)/80(74/26)
7	**4d**	*a*	9−10 h	78/22(0/100)	3−6 h	7(0/100)/93(74/26)
8	**4e**	*a*	52−55 h	81/19(0/100)	10−15 h	6(0/100)/94(81/19)
9	**4f**	*a*	14−15 h	71/29(0/100)	9−10 h	9(0/100)/91(76/24)
10[i]	**4f**	*a*	14−15 h	68/32(0/100)	7−8 h	10(0/100)/90(74/26)
11	**4f**	*b*	16−17 h	50/50(21/79)	13−14 h	18(19/81)/82(86/14)
12	**4g**	*a*	<40 min	89/11(0/100)	<40 min	8(0/100)/92(60/40)
13[j]	**4g**	*a*	<40 min	91/9(0/100)	<40 min	7(0/100)/93(63/37)
14	**4g**	*b*	<40 min	70/30(0/100)	60−80 min	15(0/100)/85(70/30)

[a] **2** (0.020 mmol), **4** (0.022 mmol) under N_2 atmosphere at 25 °C. [b] *a*, C_6D_6; *b*, CD_2Cl_2. [c] Required to reach the equilibrium of **5**/**6**. [d] Ratio at equilibrium. [e] Required to reach the equilibrium of **6**/**7**. [f] It was not clear when equilibrium was reached. [g] 99.5% of **5a** and 0.5% of **7a** after 3 h. [h] 98.9% of **5a**, 0.4% of **6a**, and 0.7% of **7a** after 3 h. [i] 4.3 equiv of **4f**. [j] 4.8 equiv of **4g**.

$$\underset{}{trans\text{-}\mathbf{3a}} + \underset{\mathbf{8}}{p\text{-MeC}_6\text{H}_4\text{SNa}} \xrightarrow[\text{CD}_2\text{Cl}_2 \; 25\,°\text{C},\ 17\text{ h}]{} \underset{79\%}{\mathbf{5a}} + \underset{0.6\%}{trans\text{-}\mathbf{6a}} + \underset{13\%\ (77/23)}{\mathbf{7a}\ (syn/anti)} \qquad (2)$$

equilibrium between **5a** and **6a** strongly leaned to the former side. When **4b** (***A*** = Me, ***B*** = H) was employed, the signal of starting **2** also completely disappeared and the formation of a mixture of the corresponding **5b**, **6b**, and **7b** was confirmed in 78%, 4.4% (*cis*/*trans* = 9/91), and 17% (*syn*/*anti* = 47/53) yields after 20 min in C_6D_6 and in 66%, 20% (*cis*/*trans* = 45/55), and 14% (*syn*/*anti* = 51/49) yields in CD_2Cl_2. Monitoring the reactions by ^{31}P NMR spectra suggested that **6b** and **7b** were produced via **5a** and revealed that the equilibria among **5b**, **6b**, and **7b** were attained in the periods of 3−4 h in C_6D_6 and 5−6 h in CD_2Cl_2 (runs 3 and 4).[7,8] The reactions using **4c** (***A*** = H, ***B*** = Me) also showed the formation of **5c**, **6c**, and **7c** after 20 min. It must be noted that the transformation from **5c** into **6c** and **7c** was much faster than that from **5b** into **6b** and **7b**; the equilibria were attained within 40 min (runs 5 and 6). The foregoing facts demonstrate that the reaction systems of **4**, possessing p-MeC$_6$H$_4$S, with **2** are quite flexible and the position changes of the equilibrium states caused by substituents and solvents are readily analyzable.

Furthermore, the comparison of the equilibria of **5b**/**6b** = 51/49 (run 3) with **5c**/**6c** = 57/43 (run 5) in C_6D_6 or **5b**/**6b** = 22/78 (run 4) with **5c**/**6c** = 17/83 (run 6) in CD_2Cl_2 indicates that the slow conversion of **5b** into **6b** and **7b** is not attributable to its thermodynamics. Moreover, it took 9−10 h and even 52−55 h to reach the equilibrium states between **5** and **6** when **4d** (***A*** = n-C$_6$H$_{13}$, ***B*** = H) and **4e** (***A*** = i-Pr, **B** = H) were employed as starting substrates, respectively (runs 7 and 8). It is also a noteworthy fact that **6**/**7** reached equilibrium states faster than **5**/**6** in these reaction systems (3−6 h vs 9−10 h in run 7 and 10−15 h vs 52−55 h in run 8). Although a larger thermodynamic driving force toward the oxidative addition from **5** to **6** was supplied by placing Ph at ***A*** compared to Ph at ***B*** (**5f**/**6f** = 71/29 of run 9 vs **5g**/**6g** = 89/11 of run 12 in C_6D_6 or **5f**/**6f** = 50/50 of run 11 vs **5g**/**6g** = 70/30 of run 14 in CD_2Cl_2), a much more prolonged time was again required to reach the equilibria; only <40 min were required for **5g**/**6g** in both C_6D_6 and CD_2Cl_2 (runs 12 and 14), while the systems of **5f**/**6f** came to equilibria during 14−15 h and 16−17 h, after the equilibria of **6f**/**7f** were achieved during the period of 9−10 h and 13−14 h, respectively (runs 9 and 11). Although there are the plural equilibrium systems such as **6**/**7**, *cis*-**6**/*trans*-**6**, and *syn*-**7**/*anti*-**7**, all the results above indicate that introducing a bulky substituent at ***A*** causes retardation of the process of conversion of **5** into **6**. The reactions performed in the presence of an excess amount of **4** toward **2** (runs 10 and 13) in the case of ***A*** = Ph or ***B*** = Ph showed no practical influence on both the reaction rates and the positions of equilibria, indicating that the generation of **6** from **5** is a unimolecular process. The chart of the ^{31}P NMR spectrum of the reaction of **4c** (***A*** = H, ***B*** = Me) with **2** in toluene-d_8 attempted at a low reaction temperature (−70 °C after 10 min) suggested the formation of two π-complexes at (a) δ 29.9 (d, J_{P-P} = 44 Hz, J_{Pt-P} = 4208 Hz) and δ 31.2 (d, J_{P-P} = 44 Hz, J_{Pt-P} = 3373 Hz) and (b) δ 29.4 (d, J_{P-P} = 41 Hz, J_{Pt-P} = 3280 Hz) and δ 30.1 (d, J_{P-P} = 41 Hz, J_{Pt-P} = 4212 Hz) in a ratio of 63/37 in 19% yields (eq 3), although the



	s-*cis*-**5c** + s-*trans*-**5c**	*trans*-**6c**	**7c** (*syn*/*anti*)
- 70 °C, 10 min	19% (63/37)	0%	0%
- 10 °C, 10 min	92% (96/4)	5%	3% (67/33)
0 °C, 10 min	74% (100/0)	11%	14% (79/21)
25 °C, 10 min	9% (100/0)	4%	87% (61/39)

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(7) The reactions were continuously monitored until the equilibria were fully achieved.

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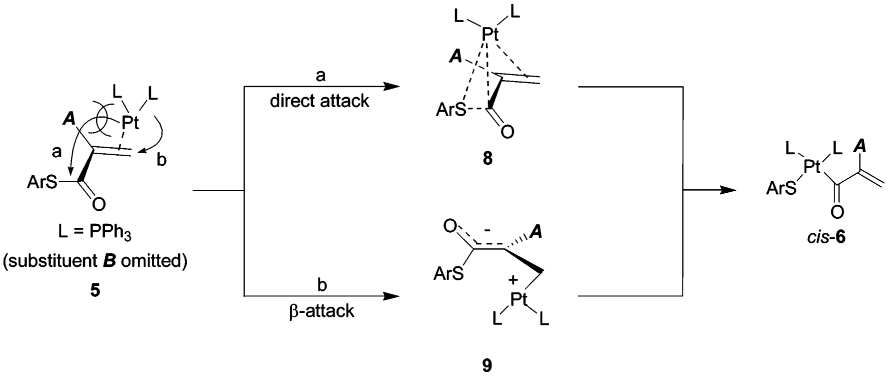
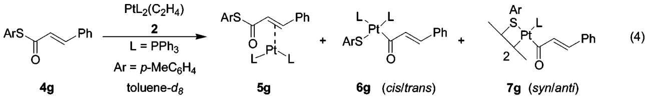
Scheme 1. Proposed Pathway from 5 to 6



stereochemistry was not able to be determined from these spectral data.[9] Then the ratio of the latter signal decreased at −10 °C (96/4) and completely disappeared at 0 °C. Eventually, **7c** was produced as a major product at 25 °C. Only the *trans* isomer of **6c** was detected during the course of this reaction. On the other hand, the reaction utilizing **4g** (***A*** = H, ***B*** = Ph) produced only one π-complex in 22% yield at −50 °C (eq 4). In this case, however, *cis*-**6g** was also detected at −30 °C (5% with *cis*/*trans* = 60/40) and *trans*-**6g** (4%) was again finally produced, indicating *cis*-**6g** was generated as a kinetic product.

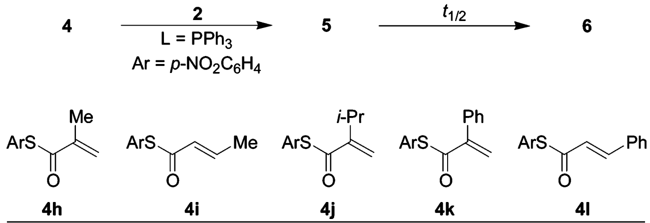


4g	toluene-d_8	5g	6g (*cis*/*trans*)		7g (*syn*/*anti*)	
	- 50 °C, 10 min	22%	0%		0%	
	- 30 °C, 10 min	63%	5%	(60/40)	0%	
	10 °C, 10 min	87%	5%	(0/100)	6.6%	(91/9)
	25 °C, 2 h	61%	4%	(0/100)	35%	(60/40)

The foregoing experimental data can be rationalized as follows (path a of Scheme 1). After the formation of π-complex **5**, the coordinated $Pt(PPh_3)_2$ fragment would approach the C−S bond with the π-coordination partially retained.[10] During the process, two PPh_3's on Pt would remain *cis*-coordinated,[4] bulky substituents at ***A*** significantly slow the reaction owing to steric hindrance, and the cleavage of the C−S bond and the formation of C−Pt and S−Pt bonds take place through a transition state such as **8**, which can possess a polarity comparable to **5**.

Other Observations. The foregoing data (Table 1) also clearly showed the following. (1) The positions of equilibria of **5**/**6** and **6**/**7** both were slightly shifted toward **6** by changing the solvent from C_6D_6 to CD_2Cl_2. (Compare 51/49 of run 3 with 22/78 of run 4 for **5b**/**6b** and 13/87 of run 3 with 22/78 of run 4 for **6b**/**7b** for instance.) That is, the conversion from **5** into **6** was thermodynamically facilitated to some degree by a polar solvent and **6** has a slightly larger dipole moment than **7**. (2) The formation of *cis*-**6** was confirmed when thioesters having the substituent at ***A*** were employed (runs 3−4 and 11), and the ratio of *cis*-**6** to *trans*-**6** was increased by changing the solvent from C_6D_6 to CD_2Cl_2. (Compare 6/94 of run 3 with 13/87 of run 4 and 0/100 of run 9 with 21/79 of run 11.) (3) The positions of equilibria between **6** and **7** were hardly influenced by the substituent at ***A*** or ***B***. The ratios of **6**/**7** were all in the narrow range from 6/94 (run 8) to 13/87 (run 3) in C_6D_6 and from 15/85 (run 14) to 22/78 in CD_2Cl_2 (run 4), indicating that the basicity of the lone pair on sulfur, which can be mainly controlled by the substituent in Ar (vide infra), was the predominant factor to determine the position of equilibria between **6** and **7**.[11] (4) The fact that the formation of *syn*-**7** over *anti*-**7** was increased by changing the solvent from C_6D_6 to CD_2Cl_2 agrees with the prediction that the dipole moment of *syn*-**7** is slightly larger than that of *anti*-**7**.

Table 2. Half-Lives from 5 to 6[a]



run	4	solvent	$t_{1/2}$ (min)	run	4	solvent	$t_{1/2}$ (min)
1	**4h**	C_6D_6	38	9[c]	**4j**	C_6D_6	43
2[b]	**4h**	C_6D_6	36	10	**4j**	CD_2Cl_2	6.8
3	**4h**	CD_2Cl_2	14	11	**4k**	C_6D_6	6.2
4	**4h**	acetone-d_6	19	12	**4k**	CD_2Cl_2	1.2
5	**4h**	THF-d_8	36	13	**4l**	C_6D_6	9.1
6	**4i**	C_6D_6	2.1	14[d]	**4l**	C_6D_6	9.1
7	**4i**	CD_2Cl_2	3.3	15	**4l**	CD_2Cl_2	7.8
8	**4j**	C_6D_6	43				

[a] **2** (0.020 mmol), **4** (0.022 mmol) under N_2 atmosphere at 25 °C. *trans*-**6** was finally predominantly produced. [b] 4.5 equiv of **4h**. [c] 5.0 equiv of **4j**. [d] 4.7 equiv of **4l**.

Reactions of Thioesters Having a *p*-$NO_2C_6H_4S$ Group with a Pt(0) Complex. It was found that more clear kinetic data from **5** to **6** were acquired by using thioesters with a *p*-$NO_2C_6H_4S$ group; monitoring the reactions of **2** with **4** shown in Table 2 demonstrated that **6** was exclusively produced from **5**, whose decay followed first-order kinetics. The fact that complexes **7** were hardly detected in these reactions (<1%) also supports the proposition that introduction of electron-withdrawing NO_2 group lowered the basicity of lone pairs on sulfur, resulting in the prevention of the formation of **7**.[11] When **4h** (***A*** = Me, ***B*** = H) was employed, the half-life of **5h** forming **6h** was calculated to be 38 min in C_6D_6 (run 1). As predicted from the results of Table 1, the introduction of Me at ***B*** kinetically facilitated the reaction (run 6, $t_{1/2}$ = 2.1 min). In stark contrast, the reaction of **4j**, having an *i*-Pr group at ***A***, which significantly retarded the reaction in the case of ArS = *p*-MeC_6H_4S (run 8 in Table 1), took place at a reaction rate comparable with that employing **4h** ($t_{1/2}$ = 43 min of run 8 vs $t_{1/2}$ = 38 min of run 1). Moreover,

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[9] It has been already reported that the X-ray crystallographic structure of $Pt[(PhH_2CO)(O)C(H)C{=}CH_2](PPh_3)_2$ showed the *s-cis* configuration for the C=O and C=C moieties. Chaloner, P. A.; Davies, S. E.; Hitchcock, P. B. *J. Organomet. Chem.* **1997**, *527*, 145.

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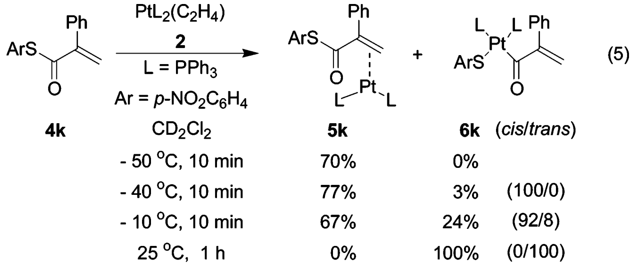
although retardation was also expected by introducing Ph at ***A*** (vide ante), the transformation of **5k** (***A*** = Ph, ***B*** = H) to **6k** was actually faster than that of **5l** (***A*** = H, ***B*** = Ph) to **6l** (6.2 min of run 11 vs 9.1 min of run 13). The effect of solvent was also very intriguing. While the reaction rates were hardly influenced by the polarity of the solvent in the cases of substrates possessing a substituent at ***B*** [2.1 min in C_6D_6 (run 6) vs 3.3 min in CD_2Cl_2 (run 7) for **5i** to **6i** or 9.1 min in C_6D_6 (run 13) vs 7.8 min in CD_2Cl_2 (run 15) for **5l** to **6l**], significant acceleration was detected in CD_2Cl_2 solution with the thioesters having a substituent at ***A***. The reactions took place 2.7 times faster for **5h** (38 min in C_6D_6 of run 1 vs 14 min in CD_2Cl_2 of run 3), 6.3 times faster for **5j** (43 min in C_6D_6 of run 8 vs 6.8 min in CD_2Cl_2 of run 10), and 5.2 times faster for **5k** (6.2 min in C_6D_6 of run 11 vs 1.2 min in CD_2Cl_2 of run 12). The reaction performed in acetone-d_6 also proceeded faster than that in C_6D_6 (19 min of run 4 vs 38 min of run 1), while no facilitation was observed in THF-d_8 (36 min of run 5). Similarly to the cases of reactions shown in Table 1, the reaction rates were independent of the excess amount of **4** in the cases of thioesters with substituents at either the ***A*** or ***B*** position [run 1 vs run 2 (4.5 equiv of **4h**), run 8 vs run 9 (5.0 equiv of **4j**), and run 13 vs run 14 (4.7 equiv of **4l**)]. When the reaction of **4k** with **2** was performed at low reaction temperature, selective formation of **5k** was confirmed at −50 °C after 10 min in 70% yield (eq 5).



4k	5k	6k	(*cis*/*trans*)
− 50 °C, 10 min	70%	0%	
− 40 °C, 10 min	77%	3%	(100/0)
− 10 °C, 10 min	67%	24%	(92/8)
25 °C, 1 h	0%	100%	(0/100)

Then *cis*-**6k** was produced at −40 °C after 10 min in 3% yield and *trans*-**6k** was quantitatively provided at 25 °C.

Unlike the cases of reactions of thioesters possessing a p-MeC$_6$H$_4$S group with **2**, the above experimental data can be rationalized by assuming that the Pt(PPh$_3$)$_2$ fragment can also attack the β-carbon (path b of Scheme 1) as well as the direct C−S bond attack (path a).[12] The β-attack would generate zwitterionic platinum complex **9**, having an anionic charge delocalized over the α-carbon and carbonyl group. The formation of **9** can be facilitated to a great extent by a polar solvent and a substituent with α-anion stabilization ability such as a Ph group at ***A***.[13] The steric repulsion caused between a substituent at ***A*** and the Pt(PPh$_3$)$_2$ fragment would facilitate the β-attack by pushing out the Pt(PPh$_3$)$_2$ fragment toward a less hindered β-carbon in path b. Presumably due to the cancellation by the retardation of path a and facilitation of path b by replacing Me with *i*-Pr at ***A***, no remarkable difference emerged in the half-lives of **5** between the reactions using **4h** and **4j** in C_6D_6 (run 1 vs run 8 in Table 2). On the other hand, path b would predominate in CD_2Cl_2 and the reaction utilizing **4j** would proceed faster than that utilizing **4h** (run 3 vs run 10 in Table 2). The reaction using a thioester with p-NO$_2$C$_6$H$_4$S and Ph groups at ***A*** would overwhelmingly occur via path b even in C_6D_6 solution due to the α-anion stabilization ability of Ph as well as the steric repulsion between Ph and the Pt(PPh$_3$)$_2$ fragment. This is why the reaction of **4k** took place faster than that of **4l** even in C_6D_6 (run 11 vs run 13 in Table 2). After the generation of **9**, the Pt(PPh$_3$)$_2$ fragment would migrate from the β-carbon to the carbonyl carbon through an $\eta^1-\eta^3-\eta^1$ type isomerization mechanism. During the process, the two PPh$_3$'s on Pt also would retain a *cis* configuration to give *cis*-**6** as a kinetic product, which would isomerize into the thermodynamically more stable *trans*-**6**.

Table 3. Activation Parameters from 5h to 6h, from 5j to 6j, and 5h from 6h

from **5h** to **6h** (***A*** = Me, ***B*** = H)	
in C_6D_6	in CD_2Cl_2
$\Delta G^\ddagger = 93.0 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 95.3 \pm 0.4$ kJ mol^{-1} $\Delta S^\ddagger = 7.5 \pm 1.4$ J K^{-1}mol^{-1}	$\Delta G^\ddagger = 90.5 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 53.5 \pm 0.1$ kJ mol^{-1} $\Delta S^\ddagger = -124.4 \pm 0.2$ J K^{-1}mol^{-1}
from **5j** to **6j** (***A*** = *i*-Pr, ***B*** = H)	
in C_6D_6	in CD_2Cl_2
$\Delta G^\ddagger = 93.4 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 78.7 \pm 0.1$ kJ mol^{-1} $\Delta S^\ddagger = 049.2 \pm 0.3$ J K^{-1}mol^{-1}	$\Delta G^\ddagger = 88.9 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 40.2 \pm 0.2$ kJ mol^{-1} $\Delta S^\ddagger = -163.5 \pm 0.5$ J K^{-1}mol^{-1}
from **5l** to **6l** (***A*** = H, ***B*** = Ph)	
in C_6D_6	in CD_2Cl_2
$\Delta G^\ddagger = 89.8 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 68.2 \pm 0.7$ kJ mol^{-1} $\Delta S^\ddagger = -72.5 \pm 2.4$ J K^{-1}mol^{-1}	$\Delta G^\ddagger = 89.5 \pm 0.1$ kJ mol^{-1} $\Delta H^\ddagger = 81.9 \pm 1.9$ kJ mol^{-1} $\Delta S^\ddagger = -25.5 \pm 6.4$ J K^{-1}mol^{-1}

To obtain more convincing information about the reaction mechanism, the activation parameters of the transformation of **6** from **5** were calculated by measuring the temperature dependence of the reaction rates (20−40 °C), and values of $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are shown in Table 3. The following facts must be noted. First, the activation parameters of the formation of **6h** from **5h** in C_6D_6 significantly differed from those in CD_2Cl_2. That is, while $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in C_6D_6 were 95.3 ± 0.4 kJ mol^{-1} and 7.5 ± 1.4 J K^{-1}mol^{-1}, those in CD_2Cl_2 were 53.5 ± 0.1 kJ mol^{-1} and −124.4 ± 0.2 J K^{-1}mol^{-1}. The large negative $\Delta S^\ddagger$ and relatively small positive $\Delta H^\ddagger$ in CD_2Cl_2 did not contradict the assumption that this reaction generates zwitterionic platinum complex **9**, where the degree of freedom of the total reaction system was significantly diminished by a polar solvent and stiff Pt−C bond formation. On the contrary, the more positive $\Delta S^\ddagger$ and larger $\Delta H^\ddagger$ in C_6D_6 suggested the loss of bond energy and only weak bond generation at the transition state. Supposing that the π-coordination and C−S bond were weakened and emerging C−Pt and S−Pt bonds were both not strong, the transition state **8** would fulfill these criteria. Second, the negative value of $\Delta S^\ddagger$ (−49.2 ± 0.3 J K^{-1} mol^{-1}) from **5j** to **6j** even in C_6D_6 also did not contradict the projection that this reaction can also proceed through path b even in C_6D_6 solution. That is, due to the significant steric hindrance caused by *i*-Pr located at ***A***, the route of path b competitively took place. The small positive $\Delta H^\ddagger$ and large negative $\Delta S^\ddagger$ in CD_2Cl_2 also accorded with the route of path b. Third, comparing the data of formation of **6l** from **5l** in C_6D_6 with those in CD_2Cl_2, differences in the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ as well as half-lives were much smaller than other cases. This can be nicely rationalized by assuming that reactions in both C_6D_6 and CD_2Cl_2 took place through a similar reaction route, namely, the

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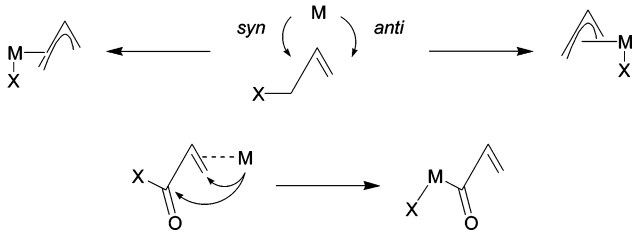
(12) It has been reported that α,β-unsaturated thioesters were employed as excellent acceptors of Michael additions. Mazery, R. D.; Pullez, M.; López, F.; Harutyunyan, S. R.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 9966, and references therein.

(13) It has been known that a substituent with an α-anion stabilization effect at the α-carbon facilitated the Michael addition of a nucleophile to α,β-unsaturated compounds. (a) Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152. (b) Holton, R. A.; Williams, A. D.; Kennedy, R. M. *J. Org. Chem.* **1986**, *51*, 5480. (c) Gawley, R. E. *Synthesis* **1976**, 777. (d) Cooke, M. P., Jr. *J. Org. Chem.* **1987**, *52*, 5729.

Scheme 2 Comparison of Oxidative Addition of Allyl−X to M with That of α,β-Unsaturated Acid Halide Derivatives to M



direct C−S bond attack of a $Pt(PPh_3)_2$ fragment (path a) from a *π*-complex.

Conclusion

When the reaction mechanism of oxidative addition of allylic halide derivatives to low-valent transition-metal complexes to generate *π*-allyl metals is considered, it has been well-established that there are two reaction routes, *syn*- and *anti*-oxidative addition (Scheme 2).[14] This study suggested that even when the substrates are α,β-unsaturated acid halide derivatives, two distinct reaction routes can similarly exist. The generality of this dual mechanism is now under investigation.

Experimental Section

General Comments. The ^{31}P and ^{1}H NMR spectra were recorded with a JEOL JMN Alice-400 spectrometer (160 and 400 MHz, respectively) in C_6D_6, CD_2Cl_2, or toluene-*d*$_8$ solution. The chemical shifts of the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4(aq) as an external standard, and $S{=}P(C_6H_4OMe\text{-}p)_3$ was used as an internal standard to calculate the yields of products. The chemical shifts in the ^{1}H NMR spectra were recorded relative to C_6H_6 (*δ* 7.15), CH_2Cl_2 (*δ* 5.32), or toluene (*δ* 2.09). IR spectra were recorded with a Perkin-Elmer FT-IR (Model 1600) spectrometer. The X-ray crystal data of *anti*-**7g** were collected by a Rigaku RAXIS-RAPID imaging plate diffractometer, and the ORTEP drawing are shown in the Supporting Information with 50% probability ellipsoids. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Acid chlorides **1a** and **1b** were commercially obtained. Thioester **4a** was prepared from the dehydrochlorination of *S*-(*p*-tolyl)-3-(chloro)propanethioate using triethylamine (*J. Am. Chem. Soc.* **1969**, *91*, 913). Thioesters **4d**−**f** were synthesized according to the literature (*Tetrahedron Lett.* **2001**, *42*, 1567). Other thioesters (**4b**,**c**, **4g**, and **4h**−**l**) were prepared from the reactions of the corresponding acid chlorides with thiols in the presence of pyridine. The platinum complex $Pt(PPh_3)_2(C_2H_4)$ (**2**) was synthesized according to the literature (*Inorg. Synth.* **1978**, *18*, 120). C_6D_6, toluene-*d*$_8$, and C_6H_6 were purified by distillation from sodium benzophenone ketyl before use. CD_2Cl_2 was distilled from CaH_2. The structures of **5**, *trans*-**6**, and **7** were determined by comparing their ^{31}P NMR chemical shifts and coupling constants (J_{P-P} and J_{Pt-P}) with those of the authentic samples **5a**, *trans*-**6l**, and **7g**.

Spectral Data of 4. 4a: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.36 (s, 3 H), 5.71 (dd, *J* = 1.6 Hz, *J* = 9.6 Hz, 1 H), 6.35 (dd, *J* = 1.6 Hz, 17.2 Hz, 1 H), 6.42 (dd, *J* = 9.6 Hz, *J* = 17.2 Hz, 1 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.4, 123.4, 126.9, 129.8, 134.1, 134.2, 139.4, 188.4; mass spectrum (EI) *m*/*z* 178 (M^+, 40); HRMS calcd for $C_{10}H_{10}OS$ 178.0452, found 178.0444. **4b**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.00 (s, 3 H), 2.37 (s, 3 H), 5.67 (s, 1 H), 6.19 (s, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 18.4, 21.5, 123.5, 123.9, 129.8, 134.7, 139.4, 143.3, 191.6; mass spectrum (EI) *m*/*z* 192 (M^+, 16); HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0611. **4c**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.88 (dd, *J* = 1.6 Hz, *J* = 7.0 Hz, 3 H), 2.36 (s, 3 H), 6.19 (dd, *J* = 1.6 Hz, *J* = 15.2 Hz, 1 H), 6.97 (dt, *J* = 7.2 Hz, *J* = 14.7 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 18.1, 21.4, 123.8, 129.1, 129.7, 134.3, 139.2, 141.5, 187.8; mass spectrum (EI) *m*/*z* 192 (M^+, 10); HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0613. **4d**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.88 (t, *J* = 6.6 Hz, 3 H), 1.29 (br, 6 H), 1.44−1.49 (m, 2 H), 2.34 (t, *J* = 7.6 Hz, 2 H), 2.38 (s, 3 H), 5.64 (s, 1 H), 6.20 (s, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 14.2, 21.5, 22.7, 28.3, 29.0, 31.7, 32.1, 122.4, 124.1, 129.8, 134.7, 139.4, 148.2, 191.9; mass spectrum (EI) *m*/*z* 262 (M^+, 14); HRMS calcd for $C_{16}H_{22}OS$ 262.1391, found 262.1393. **4e**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.11 (d, *J* = 6.8 Hz, 6 H), 2.85 (sept, *J* = 6.8 Hz, 1 H), 5.63 (s, 1 H), 6.18 (s, 1 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.3, 21.5, 29.9, 119.7, 124.1, 129.6, 134.5, 139.2, 154.3, 192.2; mass spectrum (EI) *m*/*z* 220 (M^+, 16); HRMS calcd for $C_{13}H_{16}OS$ 220.0922, found 220.0923. **4f**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.38 (s, 3 H), 5.87 (s, 1 H), 6.29 (s, 1 H), 7.22−7.45 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.9, 123.5, 124.5, 128.50, 128.55, 128.9, 130.3, 134.8, 136.0, 139.9, 148.0, 192.2; mass spectrum (EI) *m*/*z* 254 (M^+, 13); HRMS calcd for $C_{16}H_{14}OS$ 254.0765, found 254.0771. **4g**: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.38 (s, 3 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.36−7.40 (m, 5 H), 7.53−7.55 (m, 2 H), 7.66 (d, *J* = 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.5, 123.9, 124.0, 128.3, 128.8, 129.8, 130.5, 133.8, 134.3, 139.5, 141.1, 188.0; mass spectrum (EI) *m*/*z* 254 (M^+, 1); HRMS calcd for $C_{16}H_{14}OS$ 254.0765, found 254.0759. **4h**: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.03 (s, 3 H), 5.80 (s, 1 H), 6.25 (s, 1 H), 7.64 (d, *J* = 8.7 Hz, 2 H), 8.27 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 18.1, 123.5, 124.7, 134.9, 136.0, 142.8, 147.8, 188.7; mass spectrum (EI) *m*/*z* 223 (M^+, 1); HRMS calcd for $C_{10}H_9NO_3S$ 223.0303, found 223.0308. **4i**: orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.97 (d, *J* = 6.8 Hz, 3 H), 6.23 (d, *J* = 15.2 Hz, 1 H), 7.06 (dt, *J* = 6.8 Hz, *J* = 14.8 Hz, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 8.25 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 18.4, 123.7, 128.8, 134.6, 136.2, 143.6, 147.8, 185.1; mass spectrum (EI) *m*/*z* 223 (M^+, 0.4); HRMS calcd for $C_{10}H_9NO_3S$ 223.0303, found 223.0305. **4j**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 1.13 (d, *J* = 6.8 Hz, 6 H), 2.86 (sept, *J* = 6.8 Hz, 1 H), 5.75 (s, 1 H), 6.23 (s, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 8.26 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 21.7, 30.2, 121.4, 123.7, 135.0, 136.5, 147.9, 154.2, 189.6; mass spectrum (EI) *m*/*z* 251 (M^+, 0.2); HRMS calcd for $C_{12}H_{13}NO_3S$ 251.0616, found 251.0607. **4k**: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.95 (s, 1 H), 6.35 (s, 1 H), 7.39−7.45 (m, 5 H), 7.65 (d, *J* = 9.0 Hz, 2 H), 8.26 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 123.8, 124.4, 128.2, 128.3, 128.9, 134.8, 135.0, 136.4, 147.3, 148.0, 189.0; mass spectrum (EI) *m*/*z* 285 (M^+, 9.4); HRMS calcd for $C_{15}H_{11}NO_3S$ 285.0460, found 285.0547. **4l**: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.78 (d, *J* = 15.8 Hz, 1 H), 7.42−7.44 (m, 3 H), 7.57−7.59 (m, 2 H), 7.68 (d, *J* = 8.6 Hz, 2 H), 7.72 (d, *J* = 15.8 Hz, 1 H), 8.27 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 123.4, 123.7, 128.5, 128.9, 131.1, 133.4, 134.6, 136.2, 142.7, 147.9, 185.2; mass spectrum (CI) *m*/*z* 286 ($[M-H]^+$, 100); HRMS calcd for $C_{15}H_{12}NO_3S$ (M − H) 286.0538, found 286.0533.

Preparation of Authentic 5a. Into a dry two-necked reaction vessel equipped with a stirring bar were added **2** (703.0 mg, 0.94 mmol), **4a** (174.9 mg, 0.98 mmol), and C_6H_6 (3 mL). After the reaction mixture was stirred at 25 °C for 30 min, hexane (ca. 50

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[14] (a) Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.; Murai, S.; Ikeda, I. *J. Am. Chem. Soc.* **1992**, *114*, 8417, and references therein. (b) Osakada, K.; Chiba, T.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1589.

mL) was added into the mixture and the precipitate was collected by filtration. Then the solid was washed by hexane (10 mL × 3) and dried to give **5a** (672.0 mg, 80%). **5a**: mp 130 °C (a white solid); ^{1}H NMR (400 MHz, C_6D_6) δ 2.01 (s, 3 H), 2.53−2.60 (m, 1 H), 3.00−3.07 (m, 1 H), 3.90−4.06 (m, 1 H), 6.84−6.97 (m, 20 H), 7.18−7.20 (m, 2 H), 7.43−7.56 (m, 12 H); ^{31}P NMR (160 Hz, C_6D_6) δ 29.5 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 4038$ Hz), 31.4 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 3567$ Hz); IR (KBr) 3050, 1652, 1478, 1433, 1360, 1155, 1095, 967, 943, 808, 742, 692, 540, 517, 510 cm^{-1}. Anal. Calcd for $C_{46}H_{40}OP_2PtS$: C, 61.53; H, 4.49. Found: C, 61.48; H, 4.49.

Preparation of Authentic *trans*-6l. Into a dry two-necked reaction vessel equipped with a stirring bar were added **2** (747.0 mg, 1.0 mmol), **4l** (301.5 mg, 1.1 mmol), and C_6H_6 (5 mL). After the reaction mixture was stirred at 25 °C for 1.5 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The resultant solid was washed by hexane (10 mL × 3) and methanol (10 mL × 3) and then dried to give *trans*-**6l** (849.8 mg, 85%). *trans*-**6l**: mp 142 °C (orange solid); ^{1}H NMR (400 MHz, C_6D_6) δ 6.08 (d, $J = 16.0$ Hz, 1 H), 6.82−7.15 (m, 27 H), 7.47 (d, $J = 16.0$ Hz, 1 H), 7.57 (d, $J = 9.2$ Hz, 2 H), 7.80−7.83 (m, 10 H); ^{31}P NMR (160 Hz, C_6D_6) δ 16.0 (s, $J_{Pt-P} = 3228$ Hz); IR (KBr) 3056, 1580, 1566, 1493, 1482, 1435, 1319, 1094, 742, 692, 523, 514 cm^{-1}. Anal. Calcd for $C_{51}H_{41}NO_3P_2PtS$: C, 60.95; H, 4.11; N, 1.39. Found: C, 60.69; H, 4.03; N, 1.43.

Preparation of Authentic 7g. Into a dry two-necked reaction vessel equipped with a stirring bar were added **2** (897.0 mg, 1.2 mmol), **4g** (321.2 mg, 1.3 mmol), and C_6H_6 (5 mL). After the reaction mixture was stirred at 25 °C for 2 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The resultant solid was washed by hexane (10 mL × 3) and methanol (10 mL × 3) and then dried to give **7g** (394.9 mg, 46%, *syn*/*anti* = 61/39). A suitable crystal of *anti*-**7g** for X-ray crystallographic analysis was prepared by recrystallization from CH_2Cl_2/pentane at 25 °C. **7g** (the following data were collected from a mixture of stereoisomers): mp 186 °C (yellow solid); ^{1}H NMR (160 MHz, C_6D_6) (*syn* isomer) δ 1.65 (s, 3 H), 2.11 (s, 3 H), 6.13 (d, $J = 16.0$ Hz, 1 H), 6.50 (d, $J = 7.6$ Hz, 2 H), 6.58 (d, $J = 8.0$ Hz, 2 H), 7.51 (d, $J = 8.0$ Hz, 2 H), 7.58 (d, $J = 7.6$ Hz, 2 H); (*anti* isomer) δ 1.88 (s, 6 H), 6.14 (d, $J = 16.0$ Hz, 1 H) (other peaks overlapped in the region of δ 6.83−7.15 and 7.69−7.85 were not able to be read distinctively); ^{31}P NMR (160 Hz, C_6D_6) (*syn* isomer) δ 15.0 (s, $J_{Pt-P} = 4164$ Hz); (*anti* isomer) δ 16.8 (s, $J_{Pt-P} = 4028$ Hz); IR (KBr) 3055, 1626, 1582, 1486, 1434, 1096, 758, 693, 535, 511, 498 cm^{-1}. Anal. Calcd for $C_{68}H_{58}O_2P_2Pt_2S_2$: C, 57.38; H, 4.11. Found: C, 57.66; H, 4.03.

Reaction of 1a with 2 (eq 1). Into a dry Pyrex NMR tube were added **2** (15.5 mg, 0.021 mmol), **1a** (4.0 mg, 0.044 mmol), and $S{=}P(C_6H_4OMe\text{-}p)_3$ (1.7 mg, 0.0044 mmol). Then ca. 0.5 mL of toluene-d_8 was transferred by the freeze−pump−thaw method. The ^{31}P NMR spectrum taken after 10 min at −50 °C showed the quantitative formation of acylplatinum complex **3a** (*cis*/*trans* = 57/43), which completely isomerized to the *trans* isomer at 10 °C after 10 min. No formation of π-complex $Pt[(Cl)C(O)C(H){=}CH_2](PPh_3)_2$ was observed during the course of the reaction. *cis*-**3a**: ^{31}P NMR (160 MHz, toluene-d_8) δ 15.9 (d, $J_{P-P} = 17$ Hz, $J_{Pt-P} = 4662$ Hz), 18.2 (d, $J_{P-P} = 17$ Hz, $J_{Pt-P} = 1378$ Hz). *trans*-**3a**: ^{31}P NMR (160 MHz, toluene-d_8) δ 22.2 (s, $J_{Pt-P} = 3312$ Hz).

Reaction of 1b with 2 (eq 1). The reaction of **1b** with **2** was carried out in a manner similar to the reaction of **1b** with **2**. The ^{31}P NMR spectrum taken after 10 min at −50 °C showed the quantitative formation of **3b** (*cis*/*trans* = 96/4), which completely isomerized to the *trans* isomer at 10 °C after 10 min. No formation of π-complex $Pt[(Cl)C(O)C(H){=}C(Ph)(H)\text{-}(E)](PPh_3)_2$ was observed during the course of the reaction. *cis*-**3b**: ^{31}P NMR (160 MHz, toluene-d_8) δ 15.4 (d, $J_{P-P} = 16$ Hz, $J_{Pt-P} = 4715$ Hz), 17.4 (d, $J_{P-P} = 16$ Hz, $J_{Pt-P} = 1349$ Hz). *trans*-**3b**: ^{31}P NMR (160 MHz, toluene-d_8) δ 21.0 (s, $J_{Pt-P} = 3378$ Hz).

Reaction of α,β-Unsaturated Thioester 4 with 2. General Procedure (Table 1). Into a dry Pyrex NMR tube were added **2** (0.020 mmol), **4** (0.022 mmol), $S{=}P(C_6H_4OMe\text{-}p)_3$ (0.01 mmol), and solvent (0.5 mL) under a N_2 atmosphere. The reaction was roughly monitored by ^{31}P and ^{1}H NMR spectroscopy at 25 °C to determine the time required for reaching the equilibrium state among **5**, **6**, and **7**. Then the reaction was again continuously monitored by using an automatic measuring system until the equilibrium of the system was well-achieved.

Reaction of 4a with 2 in C_6D_6 (run 1). The reaction was continuously monitored by ^{31}P and ^{1}H NMR spectroscopy using an automatic measurement program system for 3 h. The ^{31}P NMR spectrum showed the formation of **5a** and *syn*-**7a**. The reaction time and the yields of **5a** and *syn*-**7a** at the time are as follows: 20 min, 100%, 0%; 2 h, 100%, 0%; 140 min, 99.7%, 0.3%; 3h, 99.5%, 0.5%. **5a**: ^{31}P NMR (160 MHz, C_6D_6) δ 29.5 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 4038$ Hz), 31.4 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 3567$ Hz). *syn*-**7a**: ^{31}P NMR (160 MHz, C_6D_6) δ 15.0 (s, $J_{Pt-P} = 4171$ Hz).

Reaction of 4a with 2 in CD_2Cl_2 (run 2). An automatic NMR measurement program system has been used to continuously monitor the reaction for 3 h. The ^{31}P NMR spectrum showed the formation of **5a**, *trans*-**6a**, and *syn*-**7a**. The reaction time and the yields of **5a**, *trans*-**6a**, and *syn*-**7a** at the time are as follows: 20 min, 99.7%, 0.3%, 0%; 2 h, 99.4%, 0.3%, 0.3%; 140 min, 98.9%, 0.4%, 0.7%; 3 h, 98.9%, 0.4%, 0.7%. **5a**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.9 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 4060$ Hz), 30.7 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 3541$ Hz). *trans*-**6a**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.6 (s, $J_{Pt-P} = 3272$ Hz). *syn*-**7a**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.0 (s, $J_{Pt-P} = 4110$ Hz).

Reaction of 4b with 2 in C_6D_6 (run 3). An automatic NMR measurement program system was used to continuously monitor the reaction for 7 h. The ^{31}P NMR spectrum showed the formation of **5b**, **6b**, and **7b**. The reaction time, the yields of **5b**, **6b** (*cis*/*trans*), and **7b** (*syn*/*anti*), and the ratios of **5b**/**6b** and **6b**/**7b** at the time are as follows: 20 min, 78%, 4.4% (9/91), 17% (47/53), 95/5, 21/79; 40 min, 64%, 7.3% (4/96), 28% (68/32), 90/10, 21/79; 1 h, 48%, 10% (10/90), 42% (76/24), 83/17, 19/81; 2 h, 24.0%, 11.6% (5/95), 64.0% (80/20), 67/33, 15/85; 3 h, 16.0%, 11.7% (6/94), 70.0% (80/20), 58/42, 16/84; 4 h, 12.0%, 11.7% (6/94), 76.0% (79/21), 51/49, 13/87; 5 h, 12.0%, 11.5% (4/96), 76.0% (80/20), 51/49, 13/87; 6 h, 11.0%, 11.6% (5/95), 77.0% (81/19), 49/51, 13/87; 7 h, 12.0%, 11.8% (7/93), 76.0% (80/20), 50/50, 13/87. Although the ratio of **5b**/**6b** after 3 h (58/42) was different from that after 4 h (51/49), those after 4 and 7 h were virtually the same. This is why it was concluded that equilibrium between **5b**/**6b** was attained in a range of time of 3−4 h (51/49). The changes of yields between **5b** and **6b** from the early stage of this reaction indicated **6b** was produced from **5b**. The equilibrium between **6b**/**7b** was also attained in a range of time of 3−4 h (13/87). **5b**: ^{31}P NMR (160 MHz, C_6D_6) δ 28.0 (d, $J_{P-P} = 41$ Hz, $J_{Pt-P} = 3827$ Hz), 31.0 (d, $J_{P-P} = 41$ Hz, $J_{Pt-P} = 3724$ Hz). *cis*-**6b**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.7 (d, $J_{P-P} = 19$ Hz, the value of J_{Pt-P} was not readable because of low intensity), 18.4 (d, $J_{P-P} = 19$ Hz, the value of J_{Pt-P} was not readable because of low intensity). *trans*-**6b**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.4 (s, $J_{Pt-P} = 3291$ Hz). *syn*-**7b**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, $J_{Pt-P} = 4188$ Hz). *anti*-**7b**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.2 (s, $J_{Pt-P} = 4124$ Hz).

Reaction of 4b with 2 in CD_2Cl_2 (run 4). An automatic NMR measurement program system has been used to continuously monitor the reaction for 8 h. The ^{31}P NMR spectrum showed the formation of **5b**, **6b**, and **7b**. The reaction time, the yields of **5b**, **6b** (*cis*/*trans*) and **7b** (*syn*/*anti*), and the ratios of **5b**/**6b** and **6b**/**7b** at the time are as follows: 20 min, 66%, 20% (45/55), 14% (51/49), 77/23, 59/41; 40 min, 45%, 24% (24/76), 31% (69/31), 65/35, 44/56; 1 h, 33%, 26% (19/81), 41% (73/27), 56/44, 39/61; 2 h, 15%, 25% (17/83), 59% (79/21), 38/62, 30/70; 3 h, 10%, 24% (15/85), 66% (81/19), 29/71, 27/73; 4 h, 9%, 22% (12/88), 69% (82/18), 29/71, 24/76; 5 h, 7%, 21% (14/86), 72% (82/18), 25/75, 23/77; 6 h, 6%, 21% (13/87), 73% (83/17), 22/78, 22/78; 7 h, 6%, 20% (15/85), 73% (82/18), 23/77, 22/78; 8 h, 6%, 20% (14/86), 74% (82/18), 23/77, 21/79. Although the ratio of **5b**/**6b** after 5 h (25/75) was different from that after 6 h (22/78), those after 6 and 8 h were virtually the same. This is why it was concluded that equilibrium between **5b**/**6b** was attained in a range of time of 5−6 h (22/78). The changes of yields between **5b** and **6b** from the early stage of this reaction indicated **6b** was produced from **5b**. The equilibrium between **6b**/**7b** was also attained in a range of time of 5−6 h (22/78). **5b**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 27.5 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 3836$ Hz), 30.5 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 3705$ Hz). *cis*-**6b**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.7 (d, $J_{P-P} = 19$ Hz, the value of J_{Pt-P} was not readable because of low intensity), 17.5 (d, $J_{P-P} = 19$ Hz, the value of J_{Pt-P} was not readable because of low intensity). *trans*-**6b**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.1 (s, $J_{Pt-P} = 3205$ Hz). *syn*-**7b**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.5 (s, $J_{Pt-P} = 4138$ Hz). *anti*-**7b**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, $J_{Pt-P} = 4019$ Hz).

Reaction of 4c with 2 in C_6D_6 (run 5). The ^{31}P NMR spectrum showed the formation of **5c**, *trans*-**6c**, and **7c**. The reaction time, the yields of **5c**, *trans*-**6c**, and **7c** (*syn*/*anti*), and the ratios of **5c**/*trans*-**6c** and *trans*-**6c**/**7c** at the time are as follows: 20 min, 11%, 7%, 82% (63/37), 61/39, 8/92; 40 min, 8%, 6%, 86% (64/36), 57/43, 7/93; 1 h, 8%, 6%, 86% (63/37), 57/43, 7/93. Although the ratio of **5c**/*trans*-**6c** after 20 min (61/39) was different from that after 40 min (57/43), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between **5c**/*trans*-**6c** was attained within 40 min (57/43). The equilibrium between *trans*-**6c**/**7c** was also attained within 40 min (7/93). **5c**: ^{31}P NMR (160 MHz, C_6D_6) δ 29.6 (d, $J_{P-P} = 44$ Hz, $J_{Pt-P} = 4210$ Hz), 30.7 (d, $J_{P-P} = 44$ Hz, $J_{Pt-P} = 3376$ Hz). *trans*-**6c**: ^{31}P NMR (160 MHz, C_6D_6) δ 17.1 (s, $J_{Pt-P} = 3310$ Hz). *syn*-**7c**: ^{31}P NMR (160 MHz, C_6D_6) δ 15.3 (s, $J_{Pt-P} = 4208$ Hz). *anti*-**7c**: ^{31}P NMR (160 MHz, C_6D_6) δ 17.1 (s, $J_{Pt-P} = 4083$ Hz).

Reaction of 4c with 2 in CD_2Cl_2 (run 6). An automatic NMR measurement program system has been used to continuously monitor the reaction for 1 h. The ^{31}P NMR spectrum showed the formation of **5c**, *trans*-**6c**, and **7c**. The reaction time, the yields of **5c**, *trans*-**6c**, and **7c** (*syn*/*anti*), and the ratios of **5c**/*trans*-**6c** and *trans*-**6c**/**7c** at the time are as follows: 20 min, 6%, 22%, 72% (75/25), 21/79, 23/77; 40 min, 4%, 19%, 77% (74/26), 17/83, 20/80; 1 h, 4%, 18%, 78% (74/26), 18/82, 19/81. Although the ratio of **5c**/*trans*-**6c** after 20 min (21/79) was different from that after 40 min (17/83), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between **5c**/*trans*-**6c** was attained within 40 min (17/83). The equilibrium between *trans*-**6c**/**7c** was also attained within 40 min (20/80). **5c**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 29.0 (d, $J_{P-P} = 43$ Hz, the value of J_{Pt-P} was not readable because of low intensity), 30.1 (d, $J_{P-P} = 43$ Hz, the value of J_{Pt-P} was not readable because of low intensity). *trans*-**6c**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.8 (s, $J_{Pt-P} = 3313$ Hz). *syn*-**7c**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.4 (s, $J_{Pt-P} = 4158$ Hz). *anti*-**7c**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.4 (s, $J_{Pt-P} = 4027$ Hz).

Reaction of 4d with 2 in C_6D_6 (run 7). An automatic measurement program system has been used to continuously monitor the reaction for 13 h. The ^{31}P NMR spectrum showed the formation of **5d**, *trans*-**6d**, and **7d**. The reaction time, the yields of **5d**, *trans*-**6d**, and **7d** (*syn*/*anti*), and the ratios of **5d**/*trans*-**6d** and *trans*-**6d**/**7d** at the time are as follows: 20 min, 95%, 2%, 2% (100/0), 98/2, 50/50; 40 min, 87%, 2%, 11% (66/34), 98/2, 15/85; 1 h, 79%, 2%, 19% (65/35), 98/2, 10/90; 3 h, 53%, 4%, 43% (70/30), 93/7, 9/91; 6 h, 32%, 5%, 63% (74/26), 86/14, 7/93; 7 h, 28%, 5%, 67% (74/26), 85/15, 7/93; 8 h, 24%, 5%, 71% (74/26), 83/17, 7/93; 9 h, 22%, 5%, 72% (75/25), 81/19, 6/94; 10 h, 21%, 6%, 73% (76/24), 78/22, 8/92; 13 h, 18%, 5%, 77% (73/27), 78/22, 6/94. Although the ratio of **5d**/*trans*-**6d** after 9 h (81/19) was different from that after 10 h (78/22), those after 10 and 13 h were virtually the same. This is why it was concluded that equilibrium between **5d**/*trans*-**6d** was attained in a range of time of 9−10 h (78/22). These data also demonstrated that **6d** was produced from **5d**. On the other hand, equilibrium between *trans*-**6d**/**7d** was attained in a range of time of 3−6 h (7/93). **5d**: ^{31}P NMR (160 MHz, C_6D_6) δ 27.5 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 3863$ Hz), 30.5 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 3669$ Hz). *trans*-**6d**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.2 (s, $J_{Pt-P} = 3312$ Hz). *syn*-**7d**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, $J_{Pt-P} = 4177$ Hz). *anti*-**7d**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, $J_{Pt-P} = 4124$ Hz).

Reaction of 4e with 2 in C_6D_6 (run 8). An automatic measurement program system has been used to continuously monitor the reaction for 71 h. The ^{31}P NMR spectrum showed the formation of **5e**, *trans*-**6e**, and **7e**. The reaction time, the yields of **5e**, *trans*-**6e**, and **7e** (*syn*/*anti*), and the ratios of **5e**/*trans*-**6e** and *trans*-**6e**/**7e** at the time are as follows: 20 min, 99.5%, 0.5%, 0%, 99.5/0.5, 100/0; 40 min, 98.3%, 0.7%, 0.9% (100/0), 99/1, 44/56; 1 h, 96.6%, 0.7%, 2.7% (82/18), 99/1, 21/79; 6 h, 79%, 2%, 19% (80/20), 98/2, 10/90; 10 h, 65%, 3%, 32% (81/19), 96/4, 9/91; 15 h, 53%, 3%, 44% (81/19), 95/5, 6/94; 21 h, 43%, 4%, 53% (80/20), 91/9, 7/93; 25 h, 37%, 4%, 59% (81/19), 90/10, 6/94; 30 h, 32%, 4%, 64% (82/18), 89/11, 6/94; 35 h, 30%, 4%, 66% (81/19), 88/12, 6/94; 40 h, 27%, 4%, 69% (80/20), 87/13, 5/95; 47 h, 25%, 5%, 70% (82/18), 83/17, 7/93; 52 h, 23%, 5%, 72% (81/19), 82/18, 6/94; 55 h, 22%, 5%, 73% (81/19), 81/19, 6/94; 66 h, 21%, 5%, 74% (80/20), 81/19, 6/94; 71 h, 21%, 5%, 74% (81/19), 81/19, 6/94. Although the ratio of **5e**/*trans*-**6e** after 52 h (82/18) was different from that after 55 h (81/19), those after 55 and 71 h were virtually the same. This is why it was concluded that equilibrium between **5e**/*trans*-**6e** was attained in a range of time of 52−55 h (81/19). These data also demonstrated that **6e** was produced from **3e**. On the other hand, the equilibrium between *trans*-**4e**/**5e** was attained in a range of time of 10−15 h (6/94). **5e**: ^{31}P NMR (160 MHz, C_6D_6) δ 26.8 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 3867$ Hz), 30.2 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 3732$ Hz). *trans*-**6e**: ^{31}P NMR (160 MHz, C_6D_6) δ 15.8 (s, $J_{Pt-P} = 3299$ Hz). *syn*-**7e**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.4 (s, $J_{Pt-P} = 4208$ Hz). *anti*-**7e**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, $J_{Pt-P} = 4114$ Hz).

Reaction of 4f with 2 in C_6D_6 (run 9). An automatic measurement program system has been used to continuously monitor the reaction for 20 h. The ^{31}P NMR spectrum showed the formation of **5f**, *trans*-**6f**, and **7f**. The reaction time, the yields of **5f**, *trans*-**6f**, and **7f** (*syn*/*anti*), and the ratios of **5f**/*trans*-**6f** and *trans*-**6f**/**7f** at the time are as follows: 20 min, 98%, 2%, 0%, 98/2, 100/0; 40 min, 91%, 4%, 5% (60/40), 96/4, 44/56; 1 h, 86%, 5%, 9% (67/33), 95/5, 36/64; 3 h, 69%, 6%, 24% (75/25), 92/8, 20/80; 6 h, 50%, 8%, 41% (78/22), 86/14, 16/84; 7 h, 32%, 8%, 60% (78/22), 80/20, 12/88; 8 h, 29%, 8%, 63% (78/22), 78/22, 11/89; 9 h, 27%, 8%, 65% (78/22), 77/23, 11/89; 10 h, 26%, 7%, 67% (76/24), 79/21, 9/91; 11 h, 24%, 7%, 69% (76/24), 77/23, 9/91; 12 h, 21%, 7%, 72% (76/24), 75/25, 9/91; 13 h, 20%, 7%, 73% (76/24), 74/26, 9/91; 14 h, 18%, 7%, 75% (76/24), 72/28, 9/91; 15 h, 17%, 7%, 76% (76/24), 71/29, 8/92; 20 h, 14%, 6%, 80% (77/23), 70/30, 7/93. Although the ratio of **5f**/*trans*-**6f** after 14 h (72/28) was different from that after 15 h (71/29), those after 15 and 20 h were virtually the same. This is why it was concluded that equilibrium between **5f**/*trans*-**6f** was attained in a range of time of 14−15h (71/29). The changes of yields between **5f** and **6f** from the early stage of this reaction indicated **6f** was produced from **5f**. On the other hand, the equilibrium between *trans*-**6f**/**7f** was attained in a range of time of 9−10 h (9/91). **5f**: ^{31}P NMR (160 MHz, C_6D_6) δ 26.6 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 4013$ Hz), 30.1 (d, $J_{P-P} = 40$ Hz, $J_{Pt-P} = 3696$ Hz). *trans*-**6f**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.1 (s,

$J_{Pt-P} = 3259$ Hz). *syn*-**7f**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.6 (s, $J_{Pt-P} = 4141$ Hz). *anti*-**7f**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.4 (s, $J_{Pt-P} = 4081$ Hz).

Reaction of 4f with 2 Using 4.3 Equiv of 4f in C_6D_6 (run 10). An automatic NMR measurement program system has been used to continuously monitor the reaction for 20 h. The ^{31}P NMR spectrum showed the formation of **5f**, *trans*-**6f**, and **7f**. The reaction time, the yields of **5f**, *trans*-**6f**, and **7f** (*syn*/*anti*), and the ratios of **5f**/*trans*-**6f** and *trans*-**6f**/**7f** at the time are as follows: 20 min, 98%, 2%, 0%, 98/2, 100/0; 40 min, 89%, 4%, 7% (73/27), 96/4, 36/64; 1 h, 82%, 6%, 12% (71/29), 93/7, 33/67; 3 h, 57%, 8%, 35% (77/23), 88/12, 19/81; 6 h, 35%, 8%, 56% (77/23), 81/19, 13/87; 7 h, 32%, 8%, 59% (78/22), 80/20, 12/88; 8 h, 28%, 7%, 65% (74/26), 80/20, 10/90; 9 h, 25%, 8%, 67% (77/23), 76/24, 11/89; 10 h, 23%, 8%, 69% (76/24), 74/26, 10/90; 11 h, 21%, 8%, 71% (77/23), 72/28, 10/90; 12 h, 21%, 7%, 72% (76/24), 75/25, 9/91; 13 h, 19%, 8%, 73% (78/22), 70/30, 10/90; 14 h, 18%, 8%, 74% (76/24), 69/31, 10/90; 15 h, 17%, 8%, 75% (78/22), 68/32, 10/90; 20 h, 15%, 7%, 78% (76/24), 68/32, 8/92. The equilibrium between **5f** and *trans*-**6f** was attained in a range of time of 14−15 h (68/32). On the other hand, the equilibrium between *trans*-**6f** and **7f** was attained in a range of time of 7−8 h (10/90). When this result was compared with that of run 9 of Table 1, it was obvious that the time required for reaching the equilibrium was not affected by the excess amount of **4f**.

Reaction of 4f with 2 in CD_2Cl_2 (run 11). An automatic measurement program system has been used to continuously monitor the reaction for 20 h. The ^{31}P NMR spectrum showed the formation of **5f**, **6f**, and **7f**. The reaction time, the yields of **5f**, **6f** (*cis*/*trans*), and **7f** (*syn*/*anti*), and the ratios of **5f**/**6f** and **6f**/**7f** at the time are as follows: 20 min, 92%, 6% (17/83), 1.5% (60/40), 94/6, 80/20; 40 min, 88%, 9% (22/78), 2.9% (69/31), 91/9, 76/24; 1 h, 85%, 11% (19/81), 4% (68/32), 89/11, 71/29; 3 h, 55%, 19% (22/78), 26% (75/25), 75/25, 42/58; 6 h, 33%, 19% (17/83), 48% (82/18), 64/36, 28/72; 10 h, 24%, 17% (20/80), 59% (85/15), 58/42, 22/78; 11 h, 22%, 17% (20/80), 61% (85/15), 56/44, 21/79; 12 h, 20%, 16% (21/79), 64% (86/14), 55/45, 20/80; 13 h, 19%, 15% (20/80), 66% (86/14), 55/45, 19/81; 14 h, 18%, 15% (19/81), 67% (86/14), 54/46, 18/82; 15 h, 17%, 15% (19/81), 68% (86/14), 54/46, 18/82; 16 h, 16%, 15% (21/79), 69% (86/14), 53/47, 18/82; 17 h, 15%, 15% (21/79), 70% (86/14), 50/50, 18/82; 20 h, 14%, 14% (20/80), 72% (87/13), 50/50, 17/83. Although the ratio of **5f**/**6f** after 16 h (53/47) was different from that after 17 h (50/50), those after 17 and 20 h were virtually the same. This is why it was concluded that equilibrium between **5f**/**6f** was attained in a range of time of 16−17 h (50/50). The changes of yields between **5f** and **6f** from the early stage of this reaction indicated **6f** was produced from **5f**. On the other hand, the equilibrium between **5f**/**6f** was attained in a range of time of 13−14 h (18/82). **5f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 25.9 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 4037$ Hz), 29.5 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 3516$ Hz). *cis*-**6f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.2 (d, $J_{P-P} = 20$ Hz, the value of J_{Pt-P} was not readable because of low intensity), 17.2 (d, $J_{P-P} = 20$ Hz, the value of J_{Pt-P} was not readable because of low intensity). *trans*-**6f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.4 (s, $J_{Pt-P} = 3241$ Hz). *syn*-**7f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.3 (s, $J_{Pt-P} = 4079$ Hz). *anti*-**7f**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, $J_{Pt-P} = 3964$ Hz).

Reaction of 4g with 2 in C_6D_6 (run 12). The ^{31}P NMR spectrum showed the formation of **5g**, *trans*-**6g**, and **7g**. The reaction time, the yields of **5g**, *trans*-**6g**, and **7g** (*syn*/*anti*), and the ratios of **5g**/*trans*-**6g** and *trans*-**6g**/**7g** at the time are as follows: 20 min, 51%, 5%, 44% (59/41), 91/9, 9/91; 40 min, 42%, 5%, 53% (60/40), 89/11, 8/92; 1 h, 37%, 5%, 58% (64/36), 88/12, 8/92. Although the ratio of **5g**/*trans*-**6g** after 20 min (91/9) was different from that after 40 min (89/11), those after 40 min and 1 h were virtually the same. This is why it was concluded that equilibrium between **5g**/*trans*-**6g** was attained within 40 min (89/11). The equilibrium between *trans*-**6g**/**7g** was also attained within 40 min (8/92) **5g**: ^{31}P NMR (160 MHz, C_6D_6) δ 27.1 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 4134$ Hz), 27.8 (d, $J_{P-P} = 38$ Hz, $J_{Pt-P} = 3591$ Hz). *trans*-**6g**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.8 (s, $J_{Pt-P} = 3281$ Hz). *syn*-**7g**: ^{31}P NMR (160 MHz, C_6D_6) δ 15.0 (s, $J_{Pt-P} = 4171$ Hz). *anti*-**7g**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.8 (s, $J_{Pt-P} = 4022$ Hz).

Reaction of 4g with 2 Using 4.8 Equiv of 4g in C_6D_6 (run 13). An automatic NMR measurement program system has been used to continuously monitor the reaction for 1 h. The ^{31}P NMR spectrum showed the formation of **5g**, *trans*-**6g**, and **7g**. The reaction time, the yields of **5g**, *trans*-**6g**, and **7g** (*syn*/*anti*), and the ratios of **5g**/*trans*-**6g** and *trans*-**6g**/**7g** at the time are as follows: 20 min, 46%, 5%, 48% (60/40), 90/10, 9/91; 40 min, 39%, 4%, 56% (63/37), 91/9, 7/93; 1 h, 36%, 4%, 56% (63/37), 90/10, 7/93. The equilibria between **5g** and *trans*-**6g**, and *trans*-**6g** and **7g** were attained within 40 min (91/9 and 7/93). When this result was compared with that of run 12 of Table 1, it was obvious that the time required for reaching the equilibrium was not affected by the excess amount of **4g**.

Reaction of 4g with 2 in CD_2Cl_2 (run 14). An automatic NMR measurement program system has been used to continuously monitor the reaction for 3 h. The ^{31}P NMR spectrum showed the formation of **5g**, *trans*-**6g**, and **7g**. The reaction time, the yields of **5g**, *trans*-**6g**, and **7g** (*syn*/*anti*), and the ratios of **5g**/*trans*-**6g** and *trans*-**6g**/**7g** at the time are as follows: 20 min, 38%, 16%, 45% (71/29), 70/30, 26/74; 40 min, 32%, 14%, 53% (72/28), 70/30, 21/79; 60 min, 28%, 13%, 59% (71/29), 68/32, 18/82; 80 min, 26%, 11%, 63% (70/30), 70/30, 15/85; 100 min, 24%, 11%, 65% (71/29), 69/31, 14/86; 2 h, 22%, 11%, 67% (70/30), 67/33, 14/86; 140 min, 24%, 11%, 65% (72/28), 69/31, 14/86; 160 min, 24%, 11%, 65% (72/28), 69/31, 14/86; 3 h, 23%, 10%, 67% (69/31), 69/31, 13/87. The ratio of **5g**/*trans*-**6g** after 40 min (70/30) and 3 h (69/31) were virtually the same. This is why it was concluded that equilibrium between **5g** and *trans*-**6g** was attained within 40 min (70/30). On the other hand, the equilibrium between *trans*-**6g** and **7g** was attained in a range of time of 60−80 min (15/85). **5g**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.6 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 4168$ Hz), 27.1 (d, $J_{P-P} = 37$ Hz, $J_{Pt-P} = 3572$ Hz). *trans*-**6g**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.6 (s, $J_{Pt-P} = 3280$ Hz). *syn*-**7g**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 15.3 (s, $J_{Pt-P} = 4133$ Hz). *anti*-**5g**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.4 (s, $J_{Pt-P} = 3977$ Hz).

Reaction of 7g with 2.0 Equiv of PPh_3 in C_6D_6. Into a dry Pyrex NMR tube were added **7g** (*syn*/*anti* = 61/39, 14.2 mg, 0.010 mmol), PPh_3 (5.2 mg, 0.020 mmol), $S{=}P(C_6H_4OMe\text{-}p)_3$ (3.1 mg, 0.0080 mmol), and C_6D_6 (0.5 mL) under N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The ^{31}P NMR spectrum showed the formation of **5g**, *trans*-**6g**, and **7g**. The reaction time, the yields of **5g**, *trans*-**6g**, and **7g** (*syn*/*anti*), and the ratios of **5g**/*trans*-**6g** and *trans*-**6g**/**7g** at the time are as follows: 20 min, 8.0%, 0.9%, 51.0% (67/33), 90/10, 2/98; 40 min, 15%, 2%, 44% (66/34), 88/12, 4/96; 1 h, 22%, 2%, 47% (64/36), 92/8, 4/96; 3 h, 34%, 5%, 47% (66/34), 87/13, 10/90; 6 h, 35%, 5%, 47% (66/34), 88/12, 10/90. The ratios of **5g**/*trans*-**6g** and *trans*-**6g**/**7g** eventually reached 88/12 and 10/90, respectively, and were virtually the same as that of run 12 of Table 1. These results verified the equilibrium among **5g**, *trans*-**6g**, and **7g**.

Reaction of *trans*-3a with 8 (eq 2). Into a dry Pyrex NMR tube were added *trans*-**3a** (16.2 mg, 0.020 mmol), **8** (8.8 mg, 0.060 mmol), $S{=}P(C_6H_4OMe\text{-}p)_3$ (3.6 mg, 0.0094 mmol), and CD_2Cl_2 (0.5 mL) under N_2 atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. After 17 h, the ^{31}P NMR spectrum showed the formation of **5a** (79%), *trans*-**6a** (0.6%), and **7a** (13%, *syn*/*anti* = 77/23). *anti*-**7a**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 17.0 (s, $J_{Pt-P} = 4013$ Hz).

Reaction of 4c with 2 in Toluene-d_8 at Low Temperature (eq 3). Into a dry Pyrex NMR tube were added **2** (15.8 mg, 0.021 mmol), **4c** (13.2 mg, 0.069 mmol), and $S{=}P(C_6H_4OMe\text{-}p)_3$ (1.3

mg, 0.0034 mmol). Then ca. 0.5 mL of toluene-d_8 was transferred by the freeze−pump−thaw method. The ^{31}P NMR spectrum showed the formation of two π-complexes, **5c** (**5c$_1$** and **5c$_2$**), *trans*-**6c**, and **7c**. The reaction temperature and time and the yields of **2**, **5c** (**5c$_1$**/**5c$_2$**), *trans*-**6c**, and **7c** at the time are as follows: −70 °C, 10 min, 81%, 19% (63/37), 0%, 0%; −10 °C, 10 min, 0%, 92% (96/4), 5%, 3% (67/33); 0 °C, 10 min, 0%, 74% (100/0), 11%, 14% (79/21); 25 °C, 0%, 9% (100/0), 4%, 87% (61/39). **2**: ^{31}P NMR (160 MHz, toluene-d_8) δ 34.9 (s, $J_{\mathrm{Pt-P}} = 3658$ Hz). **5c$_1$**: ^{31}P NMR (160 MHz, toluene-d_8) δ 29.9 (d, $J_{\mathrm{P-P}} = 44$ Hz, $J_{\mathrm{Pt-P}} = 4208$ Hz), 31.2 (d, $J_{\mathrm{P-P}} = 44$ Hz, $J_{\mathrm{Pt-P}} = 3373$ Hz). **5c$_2$**: ^{31}P NMR (160 MHz, toluene-d_8) δ 29.4 (d, $J_{\mathrm{P-P}} = 41$ Hz, $J_{\mathrm{Pt-P}} = 3280$ Hz), 30.1 (d, $J_{\mathrm{P-P}} = 41$ Hz, $J_{\mathrm{Pt-P}} = 4212$ Hz). *trans*-**6c**: ^{31}P NMR (160 MHz, toluene-d_8) δ 17.9 (s, $J_{\mathrm{Pt-P}} = 3304$ Hz). ***syn*-7c**: ^{31}P NMR (160 MHz, toluene-d_8) δ 15.9 (s, $J_{\mathrm{Pt-P}} = 4213$ Hz). *anti*-**7c**: ^{31}P NMR (160 MHz, toluene-d_8) δ 17.8 (s, $J_{\mathrm{Pt-P}} = 4050$ Hz).

Reaction of 4g with 2 in Toluene-d_8 at Low Temperature (eq 4). Into a dry Pyrex NMR tube were added **2** (15.1 mg, 0.020 mmol), **4g** (5.7 mg, 0.022 mmol), and S═P(C$_6$H$_4$OMe-*p*)$_3$ (0.9 mg, 0.0023 mmol). Then ca. 0.5 mL of toluene-d_8 was transferred by the freeze−pump−thaw method. The ^{31}P NMR spectrum showed the formation of **5g**, **6g**, and **7g**. The reaction temperature and time and the yields of **2**, **5g**, **6g**, and **7g** at the time are as follows: −50 °C, 10 min, 78%, 22%, 0%, 0%; −30 °C, 10 min, 32%, 63%, 5% (60/40), 0%; 10 °C, 10 min, 0%, 87%, 5% (0/100), 6.6 (91/9); 25 °C, 2 h, 0%, 61%, 4% (0/100), 35% (60/40). These results clearly showed that **5g** was a kinetic product, which isomerized to *cis*-**6g** then *trans*-**6g** and **7g**. **5g**: ^{31}P NMR (160 MHz, toluene-d_8) δ 27.2 (d, $J_{\mathrm{P-P}} = 37$ Hz, $J_{\mathrm{Pt-P}} = 4124$ Hz), 28.1 (d, $J_{\mathrm{P-P}} = 37$ Hz, $J_{\mathrm{Pt-P}} = 3597$ Hz). *cis*-**6g**: ^{31}P NMR (160 MHz, toluene-d_8) δ 17.1 (d, $J_{\mathrm{P-P}} = 21$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 19.1 (d, $J_{\mathrm{P-P}} = 21$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6g**: ^{31}P NMR (160 MHz, toluene-d_8) δ 17.6 (s, $J_{\mathrm{Pt-P}} = 3277$ Hz). *syn*-**7g**: ^{31}P NMR (160 MHz, toluene-d_8) δ 15.8 (s, $J_{\mathrm{Pt-P}} = 4189$ Hz). *anti*-**7g**: ^{31}P NMR (160 MHz, toluene-d_8) δ 17.5 (s, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity).

Half-Life of the Reaction of 5h to 6h in C$_6$D$_6$ (run 1 of Table 2). The ^{31}P NMR spectrum showed the formation of **5h** and **6h**. The reaction time (the average of acquisition time) and the yields of **5h** and **6h** at the time were 20 min, 75%, 25% (*cis*/*trans* = 13/87); 30 min, 62%, 38% (*cis*/*trans* = 7/93); 40 min, 51%, 49% (*cis*/*trans* = 4/96); 50 min, 42%, 57% (*cis*/*trans* = 3/97); 60 min, 35%, 64% (*cis*/*trans* = 3/97); 70 min, 29%, 71% (*cis*/*trans* = 3/97); 80 min, 24%, 76% (*cis*/*trans* = 1/99); 120 min, 11%, 89% (*trans* only); 180 min, 4%, 96% (*trans* only); 6 h, 0%, 100% (*trans* only). The consumption rate of **5h** obeyed first-order kinetics ($\ln\{[\mathbf{5h}]_0/[\mathbf{5h}]_t\} = kt$) and the half-life was calculated to be 38 min. All reactions shown in Table 2 were carried out similarly. **5h**: ^{31}P NMR (160 MHz, C$_6$D$_6$) δ 27.6 (d, $J_{\mathrm{P-P}} = 38$ Hz, $J_{\mathrm{Pt-P}} = 3863$ Hz), 30.6 (d, $J_{\mathrm{P-P}} = 38$ Hz, $J_{\mathrm{Pt-P}} = 3683$ Hz). *cis*-**6h**: ^{31}P NMR (160 MHz, C$_6$D$_6$) δ 14.5 (d, $J_{\mathrm{P-P}} = 18$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 17.9 (d, $J_{\mathrm{P-P}} = 18$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6h**: ^{31}P NMR (160 MHz, C$_6$D$_6$) δ 15.1 (s, $J_{\mathrm{Pt-P}} = 3228$ Hz).

Half-Life of the Reaction of 5h to 6h Using 4.5 Equiv of 4h in C$_6$D$_6$ (run 2). The ^{31}P NMR spectrum showed the formation of **5h** and **6h**. The reaction time (the average of acquisition time) and the yields of **5h** and **6h** at the time were 12 min, 82%, 18% (*cis*/*trans* = 19/81); 20 min, 72%, 28% (*cis*/*trans* = 9/91); 30 min, 60%, 40% (*cis*/*trans* = 5/95); 40 min, 50%, 50% (*cis*/*trans* = 2/98); 50 min, 41%, 59% (*cis*/*trans* = 4/96); 60 min, 33%, 67% (*cis*/*trans* = 3/97); 70 min, 27%, 73% (*trans* only); 80 min, 22%, 78% (*trans* only); 120 min, 12%, 88% (*trans* only); 180 min, 3%, 97% (*trans* only); 9 h, 0%, 100% (*trans* only). The consumption rate of **5h** obeyed first-order kinetics, and the half-life was calculated to be 36 min. The present result did not contradict the idea that the transformation from **5h** to **6h** was a unimolecular process.

Half-Life of the Reaction of 5h to 6h in CD$_2$Cl$_2$ (run 3). The ^{31}P NMR spectrum showed the formation of **5h** and **6h**. The reaction time (the average of acquisition time) and the yields of **5h** and **6h** at the time were 10 min, 69%, 30% (*cis*/*trans* = 67/33); 20 min, 44%, 54% (*cis*/*trans* = 42/58); 30 min, 29%, 70% (*cis*/*trans* = 30/70); 40 min, 17%, 81% (*cis*/*trans* = 20/80); 50 min, 12%, 87% (*cis*/*trans* = 12/88); 60 min, 7%, 92% (*cis*/*trans* = 9/91); 70 min, 4%, 94% (*cis*/*trans* = 7/93); 80 min, 2%, 96% (*cis*/*trans* = 6/94); 2 h, 0%, 99% (*cis*/*trans* = 3/97). The consumption rate of **5h** obeyed first-order kinetics, and the half-life was calculated to be 14 min. **5h**: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 27.2 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 4025$ Hz), 30.0 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 3667$ Hz). *cis*-**6h**: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 14.1 (d, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{Pt-P}} = 1336$ Hz), 17.0 (d, $J_{\mathrm{P-P}} = 18$ Hz, $J_{\mathrm{Pt-P}} = 3765$ Hz). *trans*-**6h**: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 15.1 (s, $J_{\mathrm{Pt-P}} = 3225$ Hz).

Half-Life of the Reaction of 5h to 6h in Acetone-d_6 (run 4). The ^{31}P NMR spectrum showed the formation of **5h** and **6h**. The reaction time (the average of acquisition time) and the yields of **5h** and **6h** at the time were 3.0 min, 92%, 8% (*cis*/*trans* = 88/12); 4.0 min, 89%, 11% (*cis*/*trans* = 68/32); 5.0 min, 85%, 15% (*cis*/*trans* = 60/40); 6.0 min, 81%, 19% (*cis*/*trans* = 59/41); 8.0 min, 76%, 24% (*cis*/*trans* = 49/51); 18 min, 54%, 46% (*cis*/*trans* = 27/63); 20 min, 50%, 50% (*cis*/*trans* = 28/72); 30 min, 34%, 67% (*cis*/*trans* = 16/84); 40 min, 25%, 75% (*cis*/*trans* = 11/89); 50 min, 17%, 83% (*cis*/*trans* = 7/93); 60 min, 9%, 91% (*cis*/*trans* = 4/96); 70 min, 6%, 94% (*cis*/*trans* = 4/96). The consumption rate of **5h** obeyed first-order kinetics, and the half-life was calculated to be 19 min. **5h**: ^{31}P NMR (160 MHz, acetone-d_6) δ 27.8 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 3882$ Hz), 30.8 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 3672$ Hz). *cis*-**6h**: ^{31}P NMR (160 MHz, acetone-d_6) δ 15.7 (d, $J_{\mathrm{P-P}} = 19$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 19.3 (d, $J_{\mathrm{P-P}} = 19$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6h**: ^{31}P NMR (160 MHz, acetone-d_6) δ 15.8 (s, $J_{\mathrm{Pt-P}} = 3243$ Hz).

Half-Life of the Reaction of 5h to 6h in THF-d_8 (run 5). The ^{31}P NMR spectrum showed the formation of **5h** and **6h**. The reaction time (the average of acquisition time) and the yields of **5h** and **6h** at the time were 4.0 min, 98%, 2% (*cis*/*trans* = 0/100); 5.0 min, 96%, 4% (*cis*/*trans* = 0/100); 6.0 min, 95%, 5% (*cis*/*trans* = 0/100); 8.0 min, 90%, 10% (*cis*/*trans* = 31/69); 9.0 min, 89%, 11% (*cis*/*trans* = 30/70); 20 min, 74%, 26% (*cis*/*trans* = 15/85); 30 min, 63%, 37% (*cis*/*trans* = 10/90); 40 min, 52%, 48% (*cis*/*trans* = 8/92); 50 min, 40%, 60% (*cis*/*trans* = 5/95); 60 min, 34%, 66% (*cis*/*trans* = 0/100); 70 min, 28%, 72% (*cis*/*trans* = 0/100). The consumption rate of **5h** obeyed first-order kinetics, and the half-life was calculated to be 36 min. **5h**: ^{31}P NMR (160 MHz, THF-d_8) δ 29.0 (d, $J_{\mathrm{P-P}} = 37$ Hz, $J_{\mathrm{Pt-P}} = 3983$ Hz), 32.0 (d, $J_{\mathrm{P-P}} = 37$ Hz, $J_{\mathrm{Pt-P}} = 3678$ Hz). *cis*-**6h**: ^{31}P NMR (160 MHz, THF-d_8) δ 16.0 (d, $J_{\mathrm{P-P}} = 18$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 19.2 (d, $J_{\mathrm{P-P}} = 18$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6h**: ^{31}P NMR (160 MHz, THF-d_8) δ 16.5 (s, $J_{\mathrm{Pt-P}} = 3224$ Hz).

Half-Life of the Reaction of 5i to 6i in C$_6$D$_6$ (run 6). Into a dry Pyrex NMR tube were added **1** (15.0 mg, 0.020 mmol), **4i** (4.9 mg, 0.022 mmol), S═P(C$_6$H$_4$OMe-*p*)$_3$ (1.0 mg, 0.0027 mmol), and C$_6$D$_6$ (0.5 mL) under N$_2$ atmosphere. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The reaction time (the average of acquisition time) and the yields of **5i** and *trans*-**6i** at the time were 2.0 min, 8.3%, 85.7%; 2.5 min, 8.2%, 90.0%; 3.0 min, 7.8%, 92.2%; 3.5 min, 7.2%, 92.8%; 4.0 min, 5.5%, 94.5%; 4.5 min, 4.8%, 95.2%; 5.0 min, 3.6%, 96.4%; 5.5 min, 3.0%, 93.2%; 6.0 min, 2.7%, 96.8%; 6.5 min, 2.2%, 90.5%; 7.0 min, 0%, 100%. The consumption rate of **5i** obeyed first-order kinetics, and the half-life was calculated to be ca. 2.1 min. **5i**: ^{31}P NMR (160 MHz, C$_6$D$_6$)

δ 29.1 (d, $J_{\mathrm{P-P}} = 42$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 30.3 (d, $J_{\mathrm{P-P}} = 42$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6i**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.3 (s, $J_{\mathrm{Pt-P}} = 3268$ Hz).

Half-Life of the Reaction of 5i to 6i in CD_2Cl_2 (run 7). The ^{31}P NMR spectrum showed the formation of **5i** and *trans*-**6i**. The reaction time (the average of acquisition time) and the yields of **5i** and *trans*-**6i** at the time were 2.0 min, 4.6%, 95.4%; 2.5 min, 3.6%, 96.4%; 3.0 min, 3.3%, 96.7%; 3.5 min, 2.9%, 97.1%; 4.0 min, 2.6%, 97.4%; 4.5 min, 2.5%, 97.5%; 5.0 min, 2.3%, 97.7%; 5.5 min, 2.2%, 97.8%; 6.0 min, 1.8%, 98.2%; 6.5 min, 1.6%, 98.4%; 7.0 min, 0%, 100%. The consumption rate of **5i** obeyed first-order kinetics, and the half-life was calculated to be ca. 3.3 min. **5i**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 28.7 (d, $J_{\mathrm{P-P}} = 40$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 29.7 (d, $J_{\mathrm{P-P}} = 40$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6i**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.3 (s, $J_{\mathrm{Pt-P}} = 3258$ Hz).

Half-Life of the Reaction of 5j to 6j in C_6D_6 (run 8). The ^{31}P NMR spectrum showed the formation of **5j** and *trans*-**6j**. The reaction time (the average of acquisition time) and the yields of **5j** and *trans*-**6j** at the time were 10 min, 90%, 10%; 20 min, 78%, 21%; 30 min, 66%, 32%; 40 min, 57%, 42%; 50 min, 48%, 49%; 60 min, 42%, 52%; 70 min, 34%, 63%; 80 min, 29%, 68%; 24 h, 0%, 98%. The consumption rate of **5j** obeyed first-order kinetics, and the half-life was calculated to be 43 min. **5j**: ^{31}P NMR (160 MHz, C_6D_6) δ 26.5 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 3909$ Hz), 30.1 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 3697$ Hz). *trans*-**6j**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.8 (s, $J_{\mathrm{Pt-P}} = 3192$ Hz).

Half-Life of the Reaction of 5j to 6j Using 5.0 Equiv of 4j in C_6D_6 (run 9). The ^{31}P NMR spectrum showed the formation of **5j** and *trans*-**6j**. The reaction time (the average of acquisition time) and the yields of **5j** and *trans*-**6j** at the time were 5 min, 93%, 7%; 6 min, 92%, 8%; 8 min, 88%, 10%; 10 min, 85%, 13%; 20 min, 73%, 23%; 30 min, 62%, 34%; 40 min, 54%, 42%; 50 min, 45%, 50%; 60 min, 38%, 57%; 70 min, 32%, 63%; 80 min, 28%, 67%. The consumption rate of **5j** obeyed first-order kinetics, and the half-life was calculated to be 43 min, showing that the transformation from **5j** to **6j** was a unimolecular process.

Half-Life of the Reaction of 5j to 6j in CD_2Cl_2 (run 10). The ^{31}P NMR spectrum showed the formation of **5j** and **6j**. The reaction time (the average of acquisition time) and the yields of **5j** and **6j** at the time were 4 min, 72%, 28% (*cis*/*trans* = 69/31); 5 min, 63%, 37% (*cis*/*trans* = 60/40); 6 min, 60%, 40% (*cis*/*trans* = 56/44); 7 min, 56%, 44% (*cis*/*trans* = 53/47); 8 min, 51%, 47% (*cis*/*trans* = 48/52); 10 min, 43%, 54% (*cis*/*trans* = 41/59); 20 min, 15%, 79% (*cis*/*trans* = 18/82); 30 min, 5%, 92% (*cis*/*trans* = 10/90); 40 min, 0%, 97% (*cis*/*trans* = 5/95). The consumption rate of **5j** obeyed first-order kinetics, and the half-life was calculated to be 6.8 min. **5j**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.0 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 3938$ Hz), 29.8 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 3684$ Hz). *cis*-**6j**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.2 (d, $J_{\mathrm{P-P}} = 19$ Hz, $J_{\mathrm{Pt-P}} = 1311$ Hz), 17.3 (d, $J_{\mathrm{P-P}} = 19$ Hz, $J_{\mathrm{Pt-P}} = 3824$ Hz). *trans*-**6j**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.7 (s, $J_{\mathrm{Pt-P}} = 3239$ Hz).

Half-Life of the Reaction of 5k to 6k in C_6D_6 (run 11). The ^{31}P NMR spectrum showed the formation of **5k** and *trans*-**6k**. The reaction time (the average of acquisition time) and the yields of **5k** and *trans*-**6k** at the time were 2 min, 25%, 75%; 4 min, 21%, 79%; 6 min, 15%, 85%; 8 min, 12%, 88%; 10 min, 9%, 91%; 12 min, 8%, 88%; 14 min, 7%, 88%; 37 min, 0%, 100%. The consumption rate of **5k** obeyed first-order kinetics, and the half-life was calculated to be 6.2 min. **5k**: ^{31}P NMR (160 MHz, C_6D_6) δ 26.2 (d, $J_{\mathrm{P-P}} = 37$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity of the signal), 29.9 (d, $J_{\mathrm{P-P}} = 37$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity of the signal). *trans*-**6k**: ^{31}P NMR (160 MHz, C_6D_6) δ 14.8 (s, $J_{\mathrm{Pt-P}} = 3206$ Hz).

Half-Life of the Reaction of 5k to 6k in CD_2Cl_2 (run 12). The ^{31}P NMR spectrum showed the formation of **5k** and **6k**. The reaction time (the average of acquisition time) and the yields of **5k** and **6k** at the time were 2 min, 32%, 68% (*cis*/*trans* = 58/42); 4 min, 8%, 86% (*cis*/*trans* = 34/66); 5 min, 4%, 90% (*cis*/*trans* = 24/76); 6 min, 3%, 91% (*cis*/*trans* = 20/80); 7 min, 2%, 92% (*cis*/*trans* = 15/85); 20 min, 0%, 97% (*cis*/*trans* = 2/98). The consumption rate of **5k** obeyed first-order kinetics, and the half-life was calculated to be 1.2 min. **5k**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 25.7 (d, $J_{\mathrm{P-P}} = 35$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity of the signal), 29.2 (d, $J_{\mathrm{P-P}} = 35$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity of the signal). *cis*-**6k**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 13.9 (d, $J_{\mathrm{P-P}} = 19$ Hz, $J_{\mathrm{Pt-P}} = 1328$ Hz), 17.1 (d, $J_{\mathrm{P-P}} = 19$ Hz, $J_{\mathrm{Pt-P}} = 3720$ Hz). *trans*-**6k**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.6 (s, $J_{\mathrm{Pt-P}} = 3186$ Hz).

Half-Life of the Reaction of 5l to 6l in C_6D_6 (run 13). The ^{31}P NMR spectrum showed the formation of **5l** and *trans*-**6l**. The reaction time (the average of acquisition time) and the yields of **5l** and *trans*-**6l** at the time were 10 min, 41%, 59%; 20 min, 21%, 74%; 30 min, 11%, 86%; 40 min, 4%, 92%; 50 min, 2%, 95%; 60 min, 1%, 95%; 3 h, 0%, 95%. The consumption rate of **5l** obeyed first-order kinetics, and the half-life was calculated to be 9.1 min. **5l**: ^{31}P NMR (160 MHz, C_6D_6) δ 26.7 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 4178$ Hz), 27.4 (d, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{Pt-P}} = 3552$ Hz). *trans*-**6l**: ^{31}P NMR (160 MHz, C_6D_6) δ 16.0 (s, $J_{\mathrm{Pt-P}} = 3229$ Hz).

Half-Life of the Reaction of 5l to 6l Using 4.7 Equiv of 4l in C_6D_6 (run 14). The ^{31}P NMR spectrum showed the formation of **5l** and *trans*-**6l**. The reaction time (the average of acquisition time) and the yields of **5l** and *trans*-**6l** at the time were 10 min, 40%, 58%; 20 min, 23%, 75%; 30 min, 13%, 83%; 40 min, 6%, 86%; 50 min, 2%, 90%; 60 min, 1%, 94%; 70 min, 0%, 92%. The consumption rate of **5l** obeyed first-order kinetics, and the half-life was calculated to be 9.1 min. The present result did not contradict the idea that the transformation from **5l** to **6l** was a unimolecular process.

Half-Life of the Reaction of 5l to 6l in CD_2Cl_2 (run 15). The ^{31}P NMR spectrum showed the formation of **5l** and **6l**. The reaction time (the average of acquisition time) and the yields of **5l** and **6l** at the time were 10 min, 31%, 69% (*cis*/*trans* = 1/99); 20 min, 12%, 88% (*cis*/*trans* = 2/98); 30 min, 6%, 94% (*cis*/*trans* = 2/98); 40 min, 2%, 98% (*trans* only); 50 min, 0%, 100% (*trans* only). The consumption rate of **5l** obeyed first-order kinetics, and the half-life was calculated to be 7.8 min. **5l**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 26.3 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 4208$ Hz), 26.7 (d, $J_{\mathrm{P-P}} = 35$ Hz, $J_{\mathrm{Pt-P}} = 3525$ Hz). *cis*-**6l**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 14.1 (d, $J_{\mathrm{P-P}} = 19$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity), 17.8 (d, $J_{\mathrm{P-P}} = 19$ Hz, the value of $J_{\mathrm{Pt-P}}$ was not readable because of low intensity). *trans*-**6l**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 16.1 (s, $J_{\mathrm{Pt-P}} = 3217$ Hz).

Reaction of 4k with 2 in CD_2Cl_2 at Low Temperature. Into a dry Pyrex NMR tube were added **2** (15.2 mg, 0.020 mmol), **4k** (6.4 mg, 0.022 mmol), and $S{=}P(C_6H_4OMe\text{-}p)_3$ (1.1 mg, 0.0028 mmol). Then ca. 0.5 mL of CD_2Cl_2 was transferred by the freeze−pump−thaw method. The ^{31}P NMR spectrum showed the formation of **5k** and **6k**. The reaction temperature and time (the average of acquisition time) and the yields of **2**, **5k**, and **6k** (*cis*/*trans*) at the time are as follows: −50 °C, 10 min, 30%, 70%, 0%; −40 °C, 10 min, 20%, 77%, 3% (100/0); −10 °C, 10 min, 9%, 67%, 24% (92/8); 25 °C, 1 h, 0%, 0%, 100% (0/100). These results clearly showed that **5k** was a kinetic product, which selectively isomerized to *cis*-**6k** then *trans*-**6k**. **2**: ^{31}P NMR (160 MHz, CD_2Cl_2) δ 33.5 (s, $J_{\mathrm{Pt-P}} = 3617$ Hz).

Activation Parameters (Table 3). Activation parameters of the transformation of **5h** to **6h**, **5j** to **6j**, and **5l** to **6l** were calculated by measuring the temperature dependence of reaction rates in the range from 20 to 40 °C in both C_6D_6 and CD_2Cl_2 according to the equation $k = (k_BT/h)\{\exp[-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/(RT)]\}$.

Activation Parameters of the Transformation of 5h to 6h in C_6D_6. Reaction temperature and reaction rates were as follows: 298 K, 0.000307 s^{-1}; 303 K, 0.000538 s^{-1}; 308 K, 0.00112 s^{-1}; 313 K, 0.00233 s^{-1}.

Activation Parameters of the Transformation of 5h to 6h in CD_2Cl_2. Reaction temperature and reaction rates were as follows: 298 K, 0.000822 s^{-1}; 303 K, 0.00131 s^{-1}; 308 K, 0.00178 s^{-1}; 313 K, 0.00255 s^{-1}.

Activation Parameters of the Transformation of 5j to 6j in C_6D_6. Reaction temperature and reaction rates were as follows: 298 K, 0.000270 s^{-1}; 303 K, 0.000422 s^{-1}; 308 K, 0.000773 s^{-1}; 313 K, 0.00133 s^{-1}.

Activation Parameters of the Transformation of 5j to 6j in CD_2Cl_2. Reaction temperature and reaction rates were as follows: 298 K, 0.00171 s^{-1}; 303 K, 0.00194 s^{-1}; 308 K, 0.00267 s^{-1}; 313 K, 0.00408 s^{-1}.

Activation Parameters of the Transformation of 5l to 6l in C_6D_6. Reaction temperature and reaction rates were as follows: 293 K, 0.000633 s^{-1}; 298 K, 0.00127 s^{-1}; 303 K, 0.00171 s^{-1}; 308 K, 0.00267 s^{-1}.

Activation Parameters of the Transformation of 5l to 6l in CD_2Cl_2. Reaction temperature and reaction rates were as follows: 293 K, 0.000750 s^{-1}; 298 K, 0.00149 s^{-1}; 303 K, 0.00169 s^{-1}; 308 K, 0.00471 s^{-1}.

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Supporting Information Available: Complete description of the X-ray crystallographic structure determination of **7g**. Crystallographic data in CIF format are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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