"β-*Cis*-SAr Effect" on Decarbonylation from α,β-Unsaturated Acyl and Aroyl Complexes

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Supporting Information

General Comments

The ^{31}P, ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JMN Alice-400 (160 MHz, 400 MHz and 100 MHz, respectively) spectrometer. The chemical shifts in the ^{1}H spectra were recorded relative to C_6H_6 (δ 7.15), CH_2Cl_2 (δ 5.32) or $CHCl_3$ (δ 7.26). The chemical shifts in the ^{13}C spectra were recorded relative to $CHCl_3$ (δ 77.0). The chemical shifts in the ^{31}P spectra were recorded relative to 85% H_3PO_4 (aq) as an external standard and S=P(C_6H_4OMe-*p*)$_3$ was used as an internal standard to calculate the yields of products. IR spectra were recorded with a Perkin Elmer FT-IR (Model 1600) spectrometer and Jasco FT/IR-410 infrared spectrophotometer. X-ray crystal data were collected by Rigaku RAXIS-RAPID Imaging Plate diffractometer. The ORTEP drawing of **6a** in Figure 1 is shown in 50% probability ellipsoids. Elemental analyses and mass spectra were acquired at the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Thioesters (**1a** and **1c**-**d**) were prepared according to the literature (*J. Am. Chem. Soc.* **1991**, *113*, 9796). Thioesters (**9b**-**c**) were also prepared according to the literature (*Monatshefte fuer Chemie* **1965**, *96*, 182). Other thioesters (**1b**, **9a** and **9d-g**) were prepared by the reaction of the corresponding acid chlorides with thiols in the presence of pyridine in THF solution. Platinum complex Pt(PPh_3)$_2$(C_2H_4) (**5**) was prepared according to the literature (*Inorg. Synth.* **1978**, *18*, 120). Palladium complex Pd(PPh_3)$_4$ was also prepared according to the literature (*J. Chem. Soc., Perkin Trans. 1*, **2001**, 1044). C_6D_6, C_6H_6, toluene and THF were purified by distillation from sodium benzophenone ketyl before use. CD_2Cl_2 was also distilled from CaH_2.

Reaction of (*Z*)-Ph(*p*-tolS)C=CHC(O)(Stol-*p*) (1a) with Pt(PPh$_3$)$_2$(C$_2$H$_4$) (5) (eq 1): Into a dry Pyrex NMR tube were added **5** (15.0 mg, 0.020 mmol), **1a** (4.6 mg, 0.012 mmol), S=P(C_6H_4OMe-*p*)$_3$ (4.5 mg, 0.012 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 Pt[(*Z*)-C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh_3)(CO) (**7a**) and Pt[(*Z*)-C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh_3)$_2$ (**4a**). The reaction times, and the yields of **7a** and **4a** at the time were 20 min, 2%, 5% (*cis* only); 3 h, 2%, 35% (*cis*/*trans* = 97/3). On the other hand, those ^{1}H NMR spectrum showed the formation of Pt[(*Z*)-C(O)C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh_3) (**6a**) in 93% (20 min) and 62% (3 h) yield, respectively. Then additional heating of the sample at 60 °C for 2 h resulted in the formation of **6a**, **4a** and (PPh_3)[(Ph)(*p*-tolS)C=CH-(*Z*)]Pt(μ-Stol-*p*)$_2$Pt[(*Z*)-C(H)=C(Stol-*p*)(Ph)](PPh_3) (**4'a**) in 3%, 18% (*cis*/*trans* = 11/89) and 79% (*syn*/*anti* = 75/25), respectively. No signal of **6a** was detected in the ^{31}P NMR spectra during course of the reaction. The structures of **4a** and **4'a** were assigned by comparison of the ^{31}P NMR data with those of the authentic sample documented in literature (*J. Am. Chem. Soc.* **2000**, *122*, 2375) and the prepared authentic sample, respectively. The structure of **6a** was unambiguously determined by X-ray crystallographic analysis. The structure of **7a** was tentatively determined by $J_{\text{Pt-P}}$ value of ^{31}P NMR and CO stretching of IR spectrum (*vide infra*).

***cis*-4a:** ^{31}P NMR (160 MHz, C_6D_6) δ 18.7 (d, $J_{\text{P-P}}$ = 17 Hz, $J_{\text{Pt-P}}$ = 1827 Hz), 19.8 (d, $J_{\text{P-P}}$ = 17 Hz, $J_{\text{Pt-P}}$ = 3222 Hz).

***trans*-4a:** ^{31}P NMR (160 MHz, C_6D_6) δ 19.9 (s, $J_{\text{Pt-P}}$ = 3033 Hz).

Preparation of 4'a: Into a dry two-necked reaction vessel equipped with a stirring bar were added **5** (748.9 mg, 1.0 mmol), **1a** (395.8 mg, 1.1 mmol) and C_6H_6 (5 mL). After the reaction mixture was stirred at 60 °C for 31 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The solid was washed by hexane (10 mL × 3) and methanol (10 mL × 3), and dried in *vacuo* to give **4'a** (421.3 mg, 52%, *syn*/*anti* = 80/20).

4'a (the following data were collected from a mixture of stereoisomers)**:** mp 134 °C (a white solid); ^{1}H NMR (400 MHz, C_6D_6) (*syn* isomer): δ 1.92 (s, 6 H), 2.04 (s, 3 H), 2.05 (s, 3 H); (*anti* isomer): δ 1.96 (s, 6 H), 2.01 (s, 6 H). Other peaks overlapping in the region of δ 6.61-8.09 were not able to be read distinctively.; ^{31}P NMR (160 Hz, C_6D_6) (*syn* isomer): δ 15.9 (s, $J_{\text{Pt-P}}$ = 3776 Hz); (*anti* isomer): δ 18.1 (s, $J_{\text{Pt-P}}$ = 3616 Hz); IR (KBr) 3736, 3630, 3050, 2917, 1887, 1593, 1573, 1526, 1488, 1435, 1301, 1210, 1182, 1097, 1028, 1017, 999, 892, 844, 804, 744, 693, 627, 537, 513, 496, 459 cm^{-1}; Anal. Calcd for $C_{80}H_{70}P_2Pt_2S_4$: C, 59.61; H, 4.38. Found: C, 59.67; H, 4.21.

Reaction of 1a with 5 under N_2 gas Bubbling (ref 5): Into a dry Pyrex NMR tube were added **5** (15.1 mg, 0.020 mmol), **1a** (8.6 mg, 0.023 mmol), S=P(C_6H_4OMe-*p*)$_3$ (4.5 mg, 0.012 mmol), and C_6D_6 (0.5 mL) under N_2 atmosphere. Then N_2 gas was bubbled into the solution using needle of syringe during course of the reaction. The reaction was monitored by ^{31}P and ^{1}H NMR spectra at 25 °C. The reaction time, and the yields of **6a**, **7a** and **4a** were 1 h, 47%, 1%, 17% (*cis* only); 3 h, 31%, 2%, 42% (*cis* only); 6 h, 16%, 1%, 68% (*cis*/*trans* = 99/1); 10 h, 11%, 1%, 81% (*cis*/*trans* = 98/2).

Reaction of (*E*)-PhC(H)=CHC(O)(Stol-*p*) (1b) with 5: Into a dry Pyrex NMR tube were added **5** (14.6 mg, 0.020 mmol), **1b** (6.0 mg, 0.024 mmol), S=P(C_6H_4OMe-*p*)$_3$ (4.1 mg, 0.011 mmol), and C_6D_6 (0.5 mL) under N_2 atmosphere. The ^{31}P NMR spectrum taken after 3 h at 25 °C showed the formation of decarbonylation product *trans*-Pt[(*E*)-C(H)=CH(Ph)](SAr)(PPh_3)$_2$ (*trans*-**4b**) in 0.5% yield. Additional heating of the solution at 60 °C for 5 h resulted in the formation of a complicated mixture including 13% of *trans*-**4b**. The structure of *trans*-**4b** was determined by comparison of the ^{31}P NMR data with those of the prepared authentic sample.

Preparation of *trans*-4b (*J. Am. Chem. Soc.* 2002, *124*, 14324): Into a dry two-necked reaction vessel equipped with a stirring bar were added *trans*-Pt[(*E*)-C(H)=CH(Ph)](PPh_3)$_2$(Br) (**14**) (724.9 mg, 0.80 mmol), *p*-tolSNa (587.4 mg, 4.0 mmol) and acetone (5 mL). After the reaction mixture was stirred at 25 °C for 14 h, benzene (ca. 50 mL) was added and filtered. Then the resultant solution was concentrated and hexane (ca. 50 mL) was added into the mixture. The precipitate was collected by filtration, and washed by hexane (10 mL × 3) and methanol (10 mL × 3), and dried in *vacuo* to provide 479.0 mg of *trans*-**4b** (63% yield).

***trans*-4b:** mp 155 °C (an yellow solid); ^{1}H NMR (400 MHz, C_6D_6) δ 2.12 (s, 3 H), 5.89 (d, J = 17.6 Hz, 1 H), 6.88-7.03 (m, 27 H), 7.80-7.85 (m, 13 H); ^{31}P NMR (160 Hz, C_6D_6) δ 23.8 (s, $J_{\text{Pt-P}}$ = 3017 Hz); IR (KBr) 3052, 2919, 1596, 1582, 1557, 1482, 1434, 1310, 1185, 1097, 1028, 998, 804, 741, 691, 630, 511, 460, 423 cm^{-1}; Anal. Calcd for $C_{51}H_{44}P_2PtS$: C, 64.75; H, 4.69. Found: C, 64.51; H, 4.53.

Preparation of 14: Into a dry two-necked reaction vessel equipped with a stirring bar were added (*E*)-PhC(H)=CHBr (0.470 mL, 3.7 mmol), **5** (899.0 mg, 1.2 mmol) and benzene (5 mL). After the reaction mixture was stirred under reflux for 1 h, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. Then the solid was washed by hexane (10 mL × 3) and methanol (10 mL × 3), and dried in *vacuo* to give 942.7 mg of **14** (87% yield).

14: mp 202 °C (a white solid); ^{1}H NMR (400 MHz, C_6D_6) δ 5.97 (d, *J* = 16.8 Hz, 1 H), 6.48 (d, *J* = 7.6 H, 2 H), 6.96-7.01 (m, 21 H), 7.89-7.91 (m, 13 H); ^{31}P NMR (160 MHz, C_6D_6) δ 24.7 (s, $J_{\text{Pt-P}}$ = 3017 Hz); IR (KBr) 3854, 3456, 3054, 1583, 1560, 1481, 1434, 1312, 1280, 1183, 1159, 1095, 1069, 1028, 998, 964, 805, 742, 694, 619, 513, 460, 428 cm^{-1}; Anal. Calcd for $C_{44}H_{37}BrP_2Pt$: C, 58.54; H, 4.13. Found: C, 58.51; H, 4.13.

Preparation of 6a: Into a dry two-necked reaction vessel equipped with a stirring bar were added **5** (1497.8 mg, 2.0 mmol), **1a** (792.3 mg, 2.1 mmol) and C_6H_6 (3 mL). After the reaction mixture was stirred at 25 °C for 3 min, hexane (ca. 50 mL) was added into the mixture and the precipitate was collected by filtration. The solid was washed by pentane (10 mL × 3) and methanol (10 mL × 3), and dried in *vacuo*. Then recrystallization from chlorobenzene/pentane at 5 °C afforded 430.9 mg of pure **6a** (26% yield). The good crystal suitable for X-ray analysis was also obtained in a similar manner. The ^{31}P NMR spectrum taken right after the crystal was dissolved in C_6D_6 showed the existence of a mixture of **6a** and **7a** in a ratio of 92/8.

6a: mp 125 °C (a reddish brown solid); ^{1}H NMR (400 MHz, C_6D_6) δ 1.72 (s, 3 H), 2.18 (s, 3 H), 6.35 (t, $J_{\text{H-Pt}}$ = 28.8 Hz, 1H) (the other peaks were not able to be read distinctively because of overlap with those of **7a**); ^{31}P NMR (160 Hz, C_6D_6) δ 30.0 (s, $J_{\text{Pt-P}}$ = 4571 Hz); IR (KBr) 3054, 1575, 1480, 1434, 1180, 1078, 1018, 999, 808, 765, 747, 702, 692, 536, 519, 496 cm^{-1}; Anal. Calcd for $C_{41}H_{35}OPPtS_2$: C, 59.05; H, 4.23. Found: C, 59.11; H, 4.29.

Confirmation of the Structure of 7a: The IR spectrum of the sample prepared by adding **6a** (16.5 mg) into CH_2Cl_2 (0.5 mL) exhibited carbonyl stretching frequencies at 2065 cm^{-1} (weak, the region of terminal CO of **7a**) and 1581 cm^{-1} (strong, the region of acyl carbonyl of **6a**). Judging from the $J_{\text{Pt-P}}$ value and Pt-CO stretching, the structure of **7a** was tentatively assigned to be Pt[(*Z*)-C(H)=C(Stol-*p*)(Ph)](Stol-*p*)(PPh_3)(CO).

7a: ^{31}P NMR (160 MHz, C_6D_6) δ 17.5 (s, $J_{\text{Pt-P}}$ = 1737 Hz).

Monitoring of the Solution of 6a by NMR (eq 2): Into a dry Pyrex NMR tube were added **6a** (15.7 mg, 0.019 mmol), S=P(C_6H_4OMe-*p*)$_3$ (3.8 mg, 0.0098 mmol), and C_6D_6 (0.5 mL) under N_2 atmosphere. The ^{31}P NMR spectra taken at 25 °C after 6 h showed the formation of **6a**, **7a** and suspected (PPh_3)[(*Z*)-(Ph)(*p*-tolS)C=CHC(O)]Pt(μ-Stol-*p*)$_2$Pt[C(O)C(H)=C(Stol-*p*)(Ph)-(*Z*)](PPh_3) (**3'a**) in 52%, 2% and 46% (*syn*/*anti* = 43/57) yield, respectively. The structure of **3'a** was determined by comparison of the ^{31}P NMR data with those of the similar dimeric acyl platinum (PPh_3)[(*Z*)-(Ph)C(H)=CHC(O)]Pt(μ-Stol-*p*)$_2$Pt[C(O)C(H)=CH(Ph)-(*Z*)](PPh_3) (See ref 3 as a reference).

***syn*-3'a:** ^{31}P NMR (160 MHz, C_6D_6) δ 13.8 (s, $J_{\text{Pt-P}}$ = 4315 Hz).

***anti*-3'a:** ^{31}P NMR (160 MHz, C_6D_6) δ 16.0 (s, $J_{\text{Pt-P}}$ = 3822 Hz).

Reaction of 6a with Catalytic Amount of PPh_3 at 25 °C: Into a dry Pyrex NMR tube were added **6a** (17.3 mg, 0.021 mmol), PPh_3 (1.4 mg, 0.0053 mmol), S=P(C_6H_4OMe-*p*)$_3$ (0.7 mg, 0.0019 mmol) and C_6D_6 (0.5 mL) under N_2 atmosphere. The ^{31}P NMR spectra taken at 25 °C after 10 min showed the formation of *cis*-**4a** (5%)and **7a** (4%), respectively. On the other hand, ^{1}H NMR spectrum detected the signal of **6a** in 82% yield.

Reaction of 6a with PPh$_3$ at Low Temperature (ref 11): Into a dry Pyrex NMR tube were added **6a** (8.5 mg, 0.010 mmol), PPh$_3$ (4.0 mg, 0.015 mmol) and S=P(C$_6$H$_4$OMe-*p*)$_3$ (1.1 mg, 0.0029 mmol). Then ca. 0.5 mL of CD$_2$Cl$_2$ was transferred by the freeze-pump-thaw method. The ^{31}P NMR spectrum taken at -90 °C showed the signals of suspected *trans*-**3a**, **6a**, **7a** and free PPh$_3$. When the temperature was gradually raised, these signals broadened and disappeared at -40 °C, -30 °C, -80 °C, and 25 °C, respectively. The reaction temperature and the ratios of *trans*-**3a**/**6a** at the temperature were -90 °C, 88/12; -80 °C, 76/24; -70 °C, 56/44; -60 °C, 9/91; -50 °C, 8/92; -40 °C, 0/100. Due to the detection of insoluble solid, yields were not accurately calculated.

***trans*-3a:** ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 13.2 (s, $J_{\text{Pt-P}}$ = 3434 Hz).

6a: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 30.4 (s, $J_{\text{Pt-P}}$ = 4552 Hz).

7a: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ 19.3 (s, $J_{\text{Pt-P}}$ = 1731 Hz).

free PPh$_3$: ^{31}P NMR (160 MHz, CD$_2$Cl$_2$) δ -7.90 (s).

The ^{31}P NMR spectrum charts are shown below (chart 1-8).

chart 1 (-90 °C)

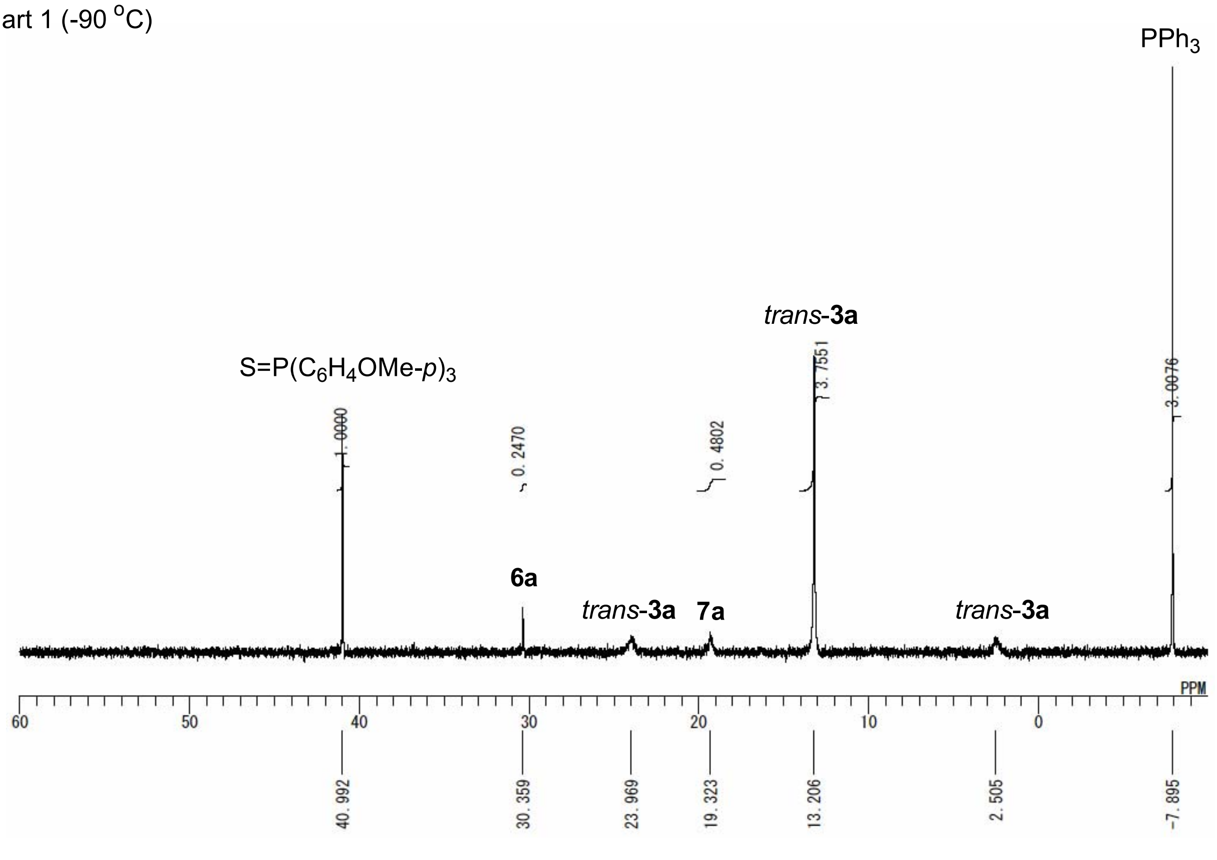


chart 2 (-80 °C)

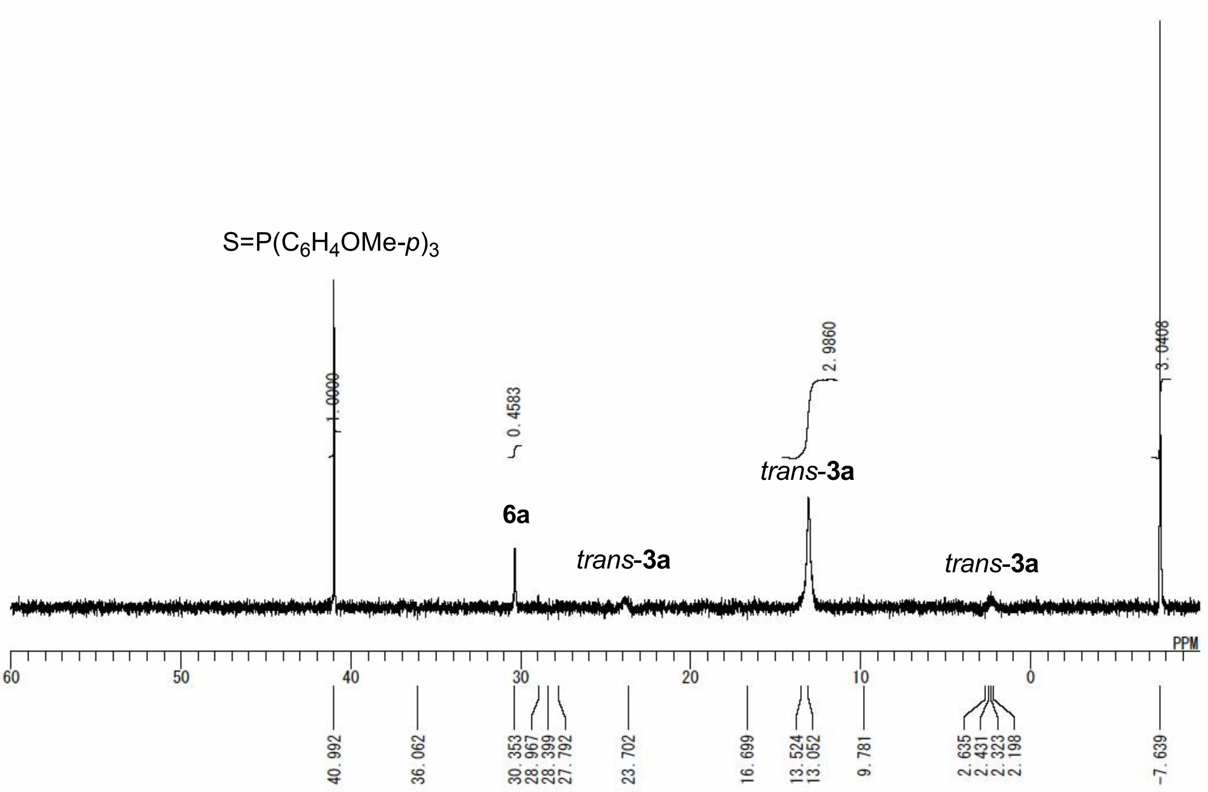


chart 3 (-70 °C)

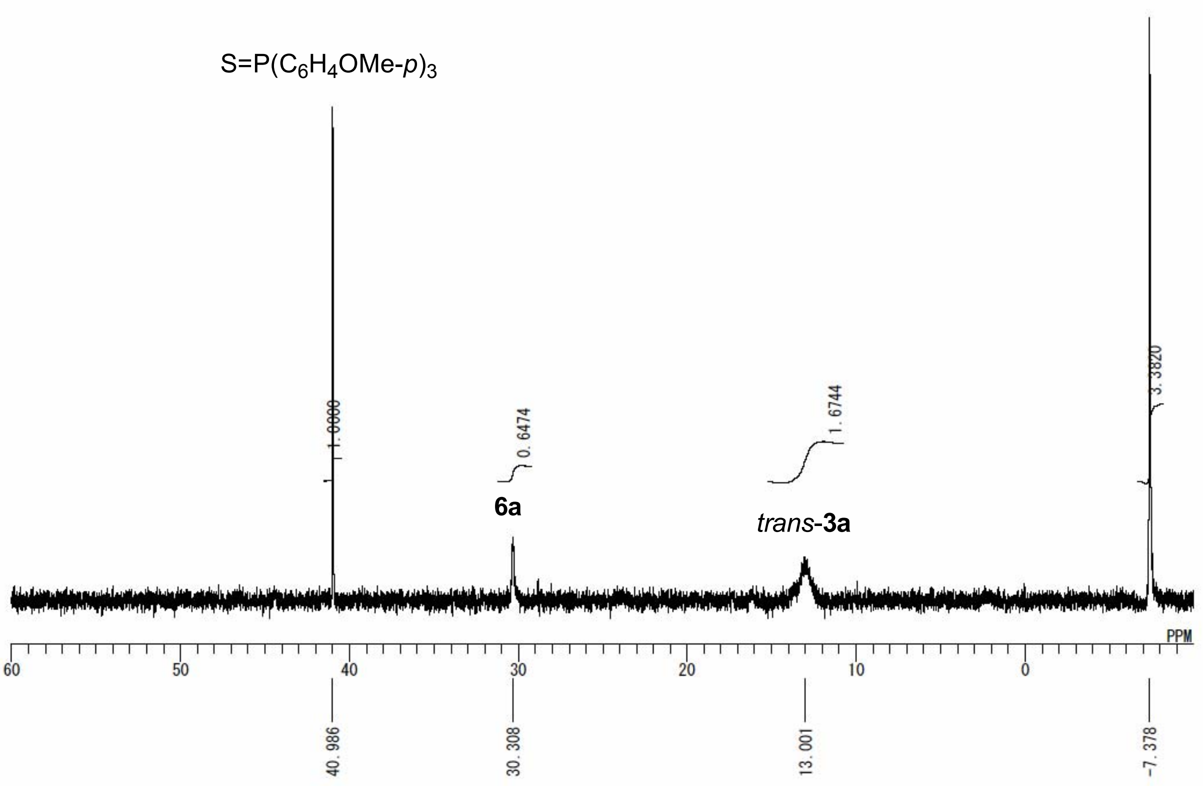


chart 4 (-60 °C)

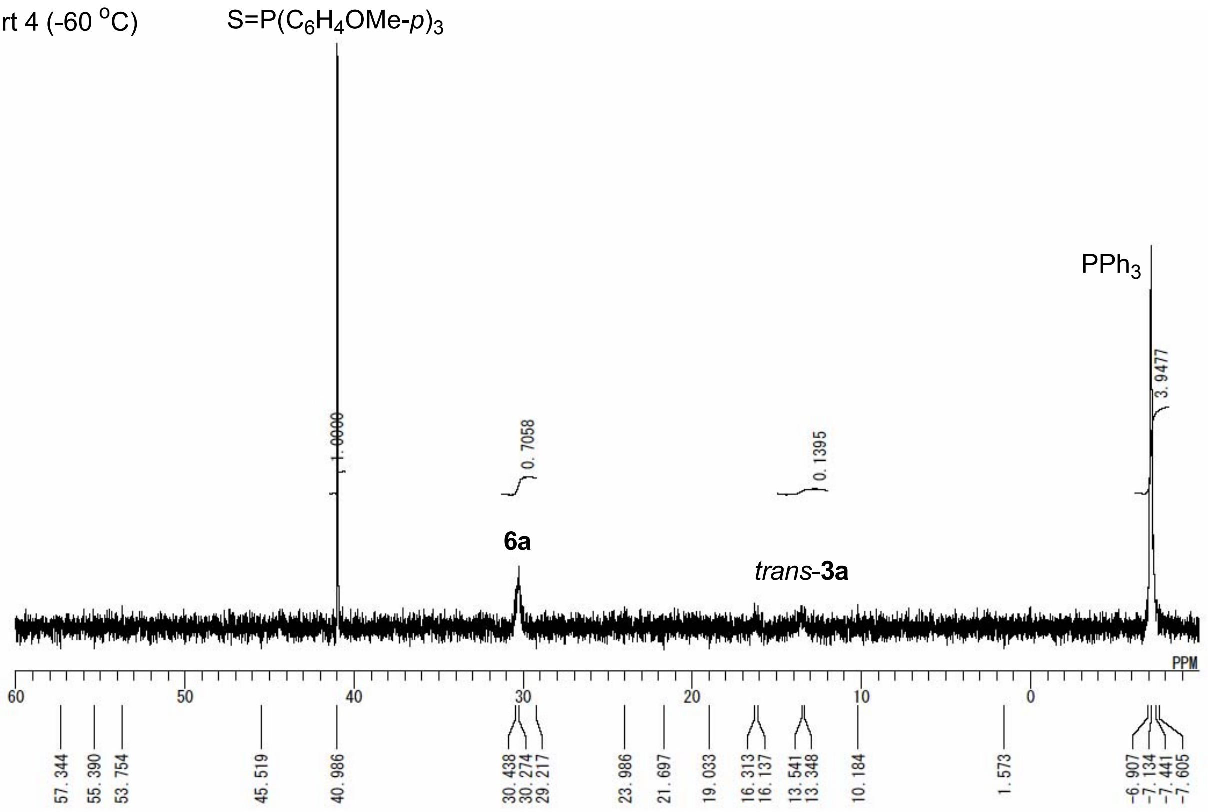


chart 5 (-50 °C)

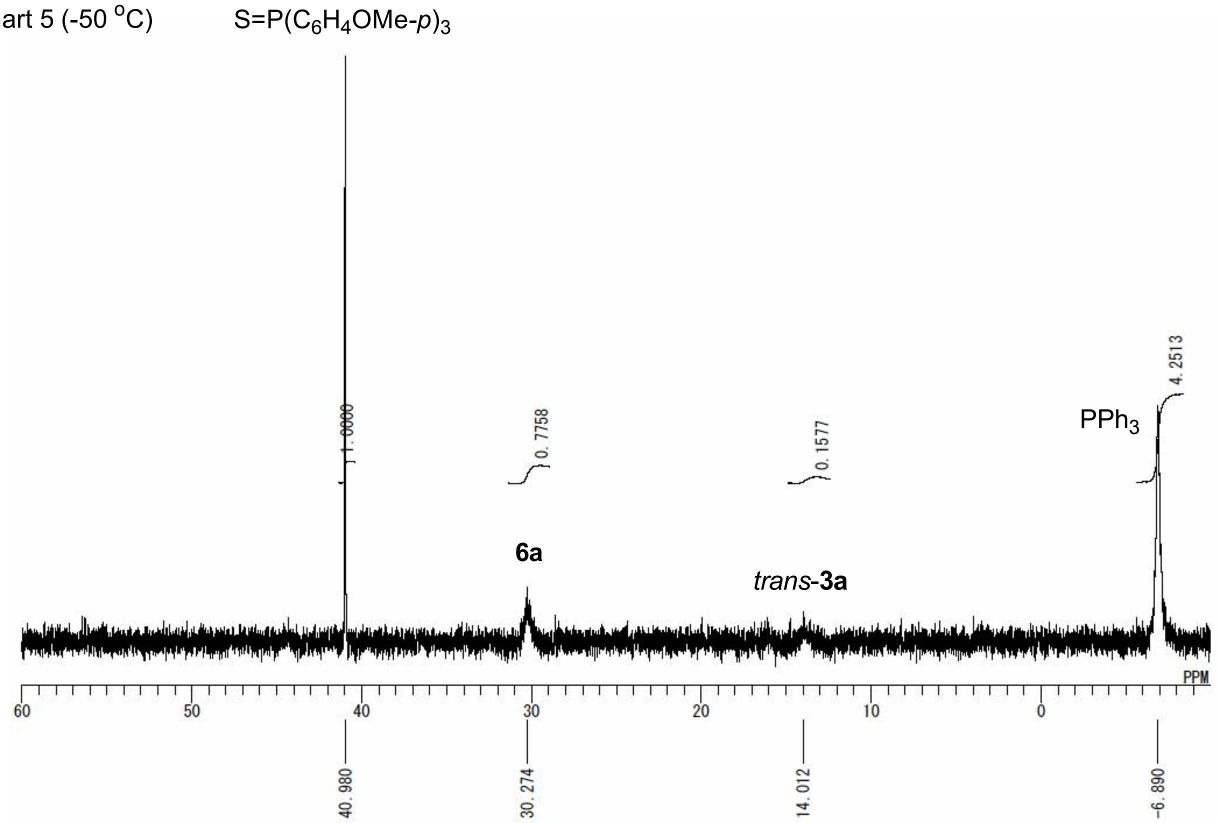


chart 6 (-40 ^{o}C)

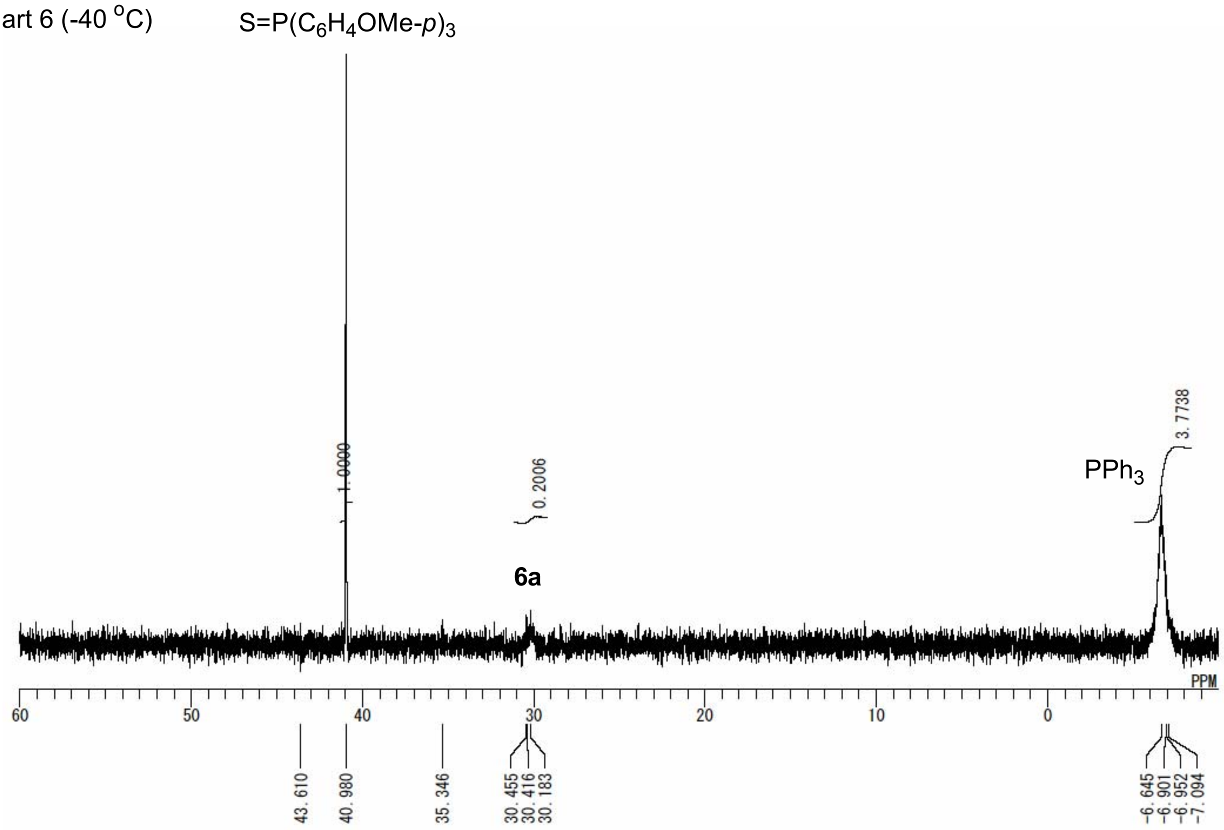


chart 7 (-30 ^{o}C)

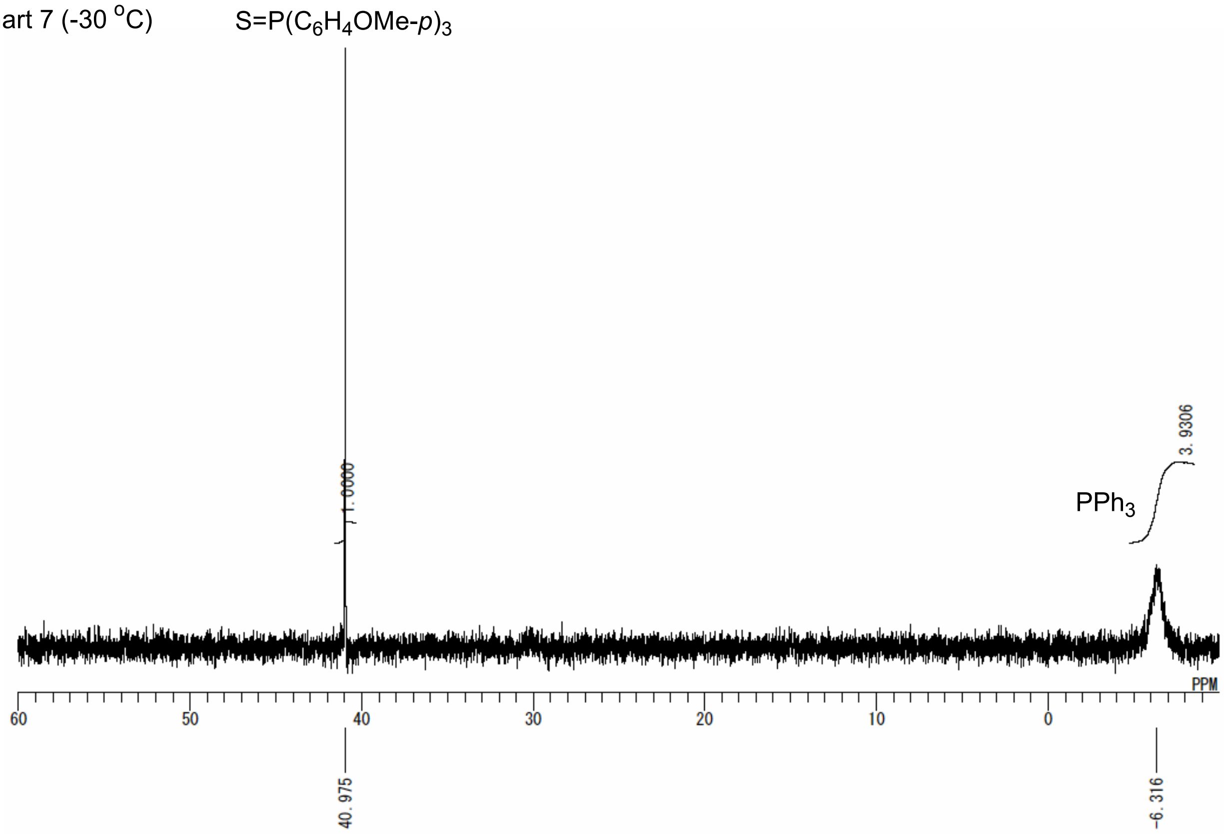
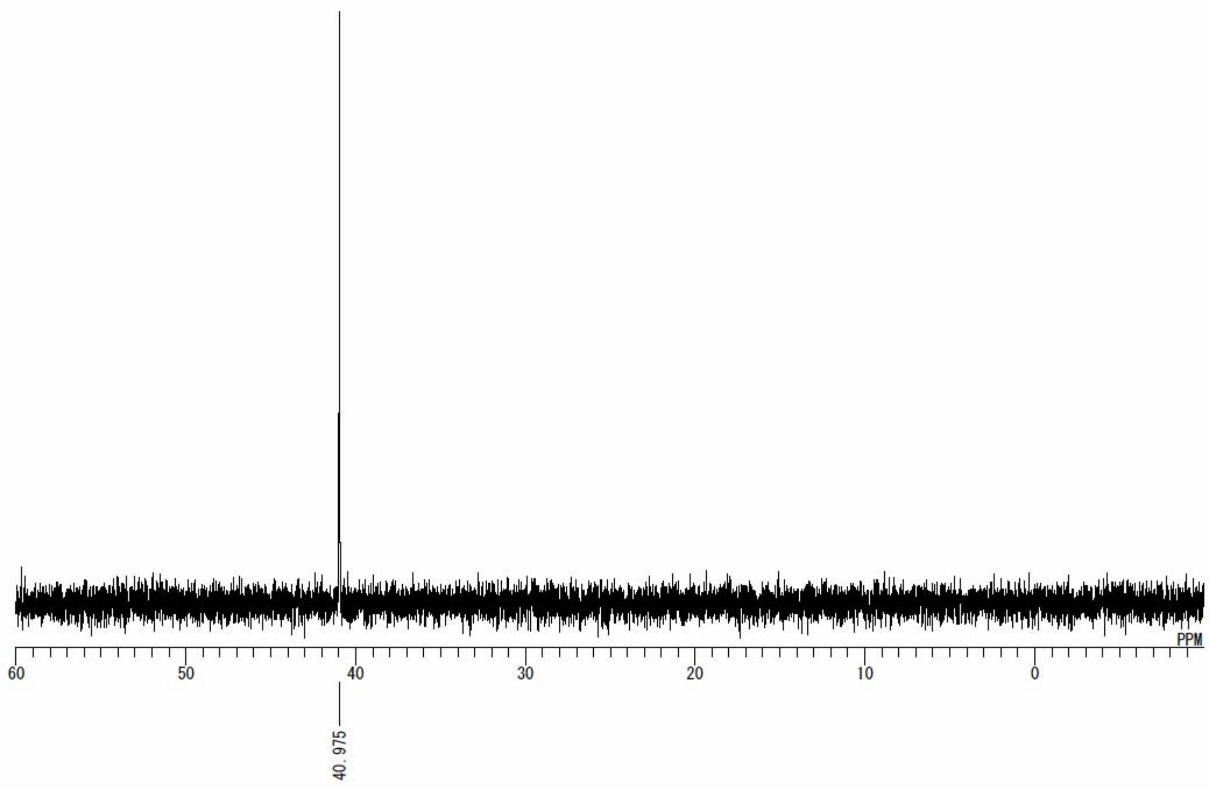


chart 8 (25 °C) $S=P(C_6H_4OMe\text{-}p)_3$



General Procedure of Palladium-Catalyzed Decarbonylation of Thioester (1) (Table 1): Into a dry flask equipped with a reflux condenser and stirring bar were added thioester (**1**) (0.50 mmol), $Pd(PPh_3)_4$ (5 mol%, 0.025 mmol) and benzene (0.5 mL). Then the solution was refluxed under a nitrogen atmosphere. After the reaction was complete, the resulting catalyst was removed by filtration through Celite and the filtrate was evaporated under reduced pressure. The residual mixture was purified by PTLC (hexane/Et_2O). Reaction time and yield of the decarbonylation products **8** were as follows.

(run 1) 8b (registry number 24182-84-1): 5 h, 0% (90% of starting **1b** was recovered).

(run 2) 8a (registry number 39654-06-3): 1 h, 98%.

(run 3) 8c (registry number 137540-56-8): 3 h, 95%.

(run 4) 8d (registry number 669723-16-4): 3 h, 6% (92% of starting **1d** was recovered).

General Procedure of Palladium-Catalyzed Decarbonylation of Thioester (9) (Table 2): All reactions were carried our in a similar way to Table 1 except for performing toluene reflux for 1 h. The yields of the decarbonylation products **10** were as follows.

(run 1) 10a (registry number 3699-01-2): 10% (90% of starting **9a** was recovered).

(run 2) 10b: 97%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3 H), 7.00-7.37 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.43, 126.60, 126.97, 127.46, 129.00, 129.97, 130.00, 130.28, 131.09, 131.88, 132.71, 134.91, 135.65, 137.73, 139.37; IR (NaCl) 3054, 2919, 1570, 1492, 1477, 1444, 1428, 1038, 811, 749, 690 cm^{-1}; mass spectrum (EI) m/z 308 (M^+, 100); Anal. Calcd for $C_{19}H_{16}S_2$: C, 73.98; H, 5.23. Found: C, 73.77; H, 5.16.

(run 3) 10c (registry number 96802-31-2): 10% (90% of starting **9c** was recovered).

(run 4) 10d (registry number 92023-43-3): 71% (29% of starting **9d** was recovered).

(run 5) 10e (registry number 22865-55-0): 13% (85% of starting **9e** was recovered).

(run 6) 10f (registry number 59345-33-4): 92%.

(run 7) 10g (registry number 6013-47-4): 3% (97% of starting **9g** was recovered).

Crystal data of 6a: space group P-1 (No. 2) with $a = 9.5969(5)$ Å, $b = 11.1578(3)$ Å, $c = 19.2187(6)$ Å, $\alpha = 83.794(2)^{\circ}$, $\beta = 89.248(5)^{\circ}$, $\gamma = 68.512(3)^{\circ}$, $Z = 2$, $\rho = 1.455$ g/cm^3, $R = 0.110$, $R_w = 0.172$.