Inorg. Chem. **2006**, *45*, 1399–1404

cis-to-trans Isomerization Promoted by Pyridine as a Crucial Step for the Selective Preparation of *trans*-Pt(SAr)(Cl)(PAr′$_3$)$_2$

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Received October 14, 2005

The general strategy for the syntheses of *trans*-Pt(SAr)(Cl)(PAr′$_3$)$_2$ (**1**) (Ar = Ph, C_6H_4-2-Me, C_6H_4-3-OMe C_6H_4-2-F, etc.; Ar′ = Ph, C_6H_4-4-OMe, C_6H_4-4-Me, and C_6H_4-4-CF_3) by the reaction of *cis*-$PtCl_2$(PAr′$_3$)$_2$ with ArSH has been developed. The mechanistic investigation suggested that isomerization of *cis*-**1** into *trans*-**1** promoted by the combined use of C_6H_6 as a solvent and pyridine as a base was the key to the successful preparation of **1**.

Introduction

Unveiling the reactivity of transition metal complexes having ArS−M (M = Pd or Pt) bonds toward unsaturated compounds is of critical importance for understanding and developing catalytic reactions using the S−X bond (X = typical element or functional group) activations[1] because many of them can involve the insertion of unsaturated organic molecules into S−M bonds. However, clear-cut investigation of the insertion process has been generally hampered by the successive reactions. For instance, we have reported that the reaction of Pd(SAr)$_2$(PPh$_3$)(CNAr) with (ArS)$_2$ (Ar = C_6H_4-4-Me) produced ArSC═NAr(SAr) and Pd(SAr)$_2$(PPh$_3$)$_n$ and that the reaction of Pt(SAr)(Ph)(PPh$_3$)$_2$ (Ar = C_6H_4-4-Br) with 1-octyne produced Pt(*n*-C_6H_{13}CCH)(PPh$_3$)$_2$ and (*Z*)-(*n*-C_6H_{13})(ArS)C═C(H)(Ph).[2,3] In both cases, possible intermediates, thioimidoyl palladium or vinyl platinum, produced by the insertion of ArNC into S−Pd or 1-octyne into S−Pt, were not detected at all. Furthermore, Tanaka et al. also showed that the reaction of *trans*-Pd(SPh)(CO_2Me)-(PCy$_3$)$_2$ with 1-octyne yielded (*Z*)-(*n*-C_6H_{13})(PhS)C═C(H)-(CO_2Me).[4] These results indicated that the C−S or C−C bond-forming reductive eliminations from Pd(II) or Pt(II) were generally much faster than the insertion of unsaturated organic compounds into the S−M (M = Pd, Pt) bonds.[5] To our knowledge, direct evidence of the insertion of unsaturated compounds into S−Pd or S−Pt bond when a catalytically active substrate was employed has not yet been provided.[6,7] We have expected that complexes with general formula Pt-(SAr)(Cl)(PAr′$_3$)$_2$ (**1**) would be versatile as substrates for scrutinization of the insertion processes because complex **1** would be thermodynamically more stable than the corresponding Pd complexes,[8] and the anticipated Pt(II) complexes, formed by the insertion of unsaturated molecules into S−Pt bond, would resist further reactions, such as the C−Cl bond-forming reductive elimination. However, with respect to the syntheses of platinum complexes with general formula

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10.1021/ic051780l CCC: $33.50
Published on Web 01/11/2006

of **1**, only very limited examples of related complexes, such as Pt(SAr)(Cl)(PPh_3)$_2$ (Ar = C_6H_2-2,4,6-*i*-Pr_3),[9a] Pt(SCF_3)-(Cl)(PPh_3)$_2$,[9b] and Pt(SPy)(Cl)(PPh_3),[9c−9e] have been documented. These publications made us feel that possible dimerization, polymerization, and disproportionation can be significant drawbacks in the preparation and handling **1**.[10] Herein, we wish to report on our discovery that complex **1** is actually quite selectively prepared as a thermodynamically stable complex using pertinent reaction conditions. The key to our success was employment of benzene, as the solvent, and pyridine, which acted not only as a base but also as a cis-to-trans isomerization catalyst.[11]

Experimental Section

General Comments. ^{1}H and ^{31}P NMR spectra in benzene-d_6 solution were recorded with a JEOL JNM-AL-400 (400 MHz) spectrometer, and their chemical shifts were recorded relative to Me_4Si and 85% (aq) H_3PO_4. IR spectra were measured with a Perkin-Elmer Model 1600 spectrometer. Combustion analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Melting points were determined on a Yanaco MICRO melting point apparatus. Preparative TLC was carried out using Wakogel B-5F silica gel using benzene as an eluent. X-ray crystal data for *trans*-**1i** were collected with a Rigaku RAXIS−RAPID Imaging Plate diffractometer, and its ORTEP drawing in Figure 1 was shown with 50% probability ellipsoids. The platinum complexes *cis*-Pt(Cl)$_2$(PR_3)$_2$ (*cis*-**2**) and *trans*-Pt(Cl)$_2$-(PPh_3)$_2$ (*trans*-**2a**) were prepared according to the literature.[12a−c] The authentic platinum complex *cis*-Pt(SPh)$_2$(PPh_3)$_2$ (*cis*-**4a**) was also synthesized according to the literature,[13] and its stereochemistry has been unambiguously identified by X-ray crystallographic analysis. The chemical shift and coupling constant of *trans*-Pt(SPh)$_2$-(PPh_3)$_2$ (*trans*-**4a**) in ^{31}P NMR spectra was determined by using the isomerization of *cis*-**4a** to *trans*-**4a**. The platinum complex *trans*-Pt(SC_6H_4-4-OMe)$_2$(PPh_3)$_2$ (**4b**) was prepared according to the literature.[10b] Thiols (**3**), pyridine, NEt_3, PPh_3, C_6D_6, C_6H_6, and CD_2-Cl_2 were commercially obtained and employed without any further purification. The ^{31}P NMR spectra were measured using standard ^{1}H-gated decoupled conditions to calculate the yields of **1a** and **4a** shown in Table 2 with S=P(C_6H_4-4-Me)$_3$ as an internal standard. The values may contain ca. 30% errors from the difference in sensitivity to NOE by ^{1}H irradiation between complexes and the internal standard. (The integrals of *trans*-**1a** and *trans*-**4a** were both 1.27 times larger than that of the internal standard under ^{1}H-coupled conditions where the PD time was set for 70 s, roughly five times longer than the relaxation time T_1 of PPh_3 (ca. 13.5 s).)

Attempted Synthesis of *trans*-1a (run 1 of Table 2). *cis*-PtCl_2-(PPh_3)$_2$ (*cis*-**2a**) (7.9 mg, 0.010 mmol), S=P(C_6H_4-4-Me)$_3$ (3.0 mg, 0.009 mmol as an internal standard), C_6D_6 (0.5 mL), PhSH (**3a**, 1.2 mg, 0.012 mmol), and Et_3N (5.0 mg, 0.05 mmol) were mixed in a Pyrex NMR tube. Then the reaction was monitored by ^{31}P and ^{1}H NMR spectra. The ^{31}P NMR spectrum showed the formation of *cis*-Pt(SPh)(Cl)(PPh_3)$_2$ (*cis*-**1a**) [δ 21.6 (J_{P-P} = 17 Hz, J_{Pt-P} = 2676 Hz), 20.1 (J_{P-P} = 17 Hz, J_{Pt-P} = 3840 Hz)] and *cis*-**4a** [δ 23.8 (s, J_{Pt-P} = 2880 Hz)] in 8 and 55% yields, respectively after 1h. Other reactions shown in Table 2 except for run 8 were carried out and the yields of the products were calculated similarly.

Synthesis of *trans*-1a (run 8 of Table 2): General Procedure for Preparation of 1. *cis*-**2a** (347 mg, 0.44 mmol), C_6H_6 (20 mL) and pyridine (0.16 mL, 2.0 mmol) were combined in a dry three-necked flask equipped with an additional flask. Then the C_6H_6 (3 mL) solution of PhSH (0.40 mmol) was added dropwise to the solution, and resultant reaction mixture was stirred for a total of 2 h. Then the reaction mixture was filtered; hexane (100 mL) was added into the filtered solution, and the resultant solid was filtered, washed over hexane, and dried under vacuo. It was then purified by PTLC using benzene as an eluent to give the desired *trans*-**1a** as a yellow solid (247 mg, 71%).

Other platinum complexes shown in Tables 4 and 5 were prepared and isolated in a similar manner.

***trans*-Pt(SPh)(Cl)(PPh_3)$_2$ (1a).** Yellow solid. mp: 212−213 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.94−7.88 (m, 12 H), 7.28 (dd, J = 8.0 Hz, J = 1.6 Hz, 2 H), 6.98−6.95 (m, 18 H), 6.67−6.61 (m, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.4 (s, J_{Pt-P} = 2745 Hz). IR (KBr): 3054, 1578, 1481, 1469, 1434, 1384, 1311, 1186, 1158, 1096, 1024, 998, 741, 705, 691, 522, 513, 414 cm^{-1}. Anal. Calcd for $C_{42}H_{35}ClP_2PtS$: C, 58.37; H, 4.08. Found: C, 58.08; H, 4.00.

***trans*-Pt(SC_6H_4-2-Me)(Cl)(PPh_3)$_2$ (1b).** Yellow solid. mp: 201−202 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.33 (d, J = 7.6 Hz, 1 H), 7.90−7.88 (m, 12 H), 6.97−6.96 (m, 18 H), 6.80 (t, J = 7.2 Hz, 1 H), 6.67 (t, J = 7.2 Hz, 1 H), 6.53 (d, J = 6.8 Hz, 1 H), 1.86 (s, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.5 (s, J_{Pt-P} = 2751 Hz). IR (KBr): 3054, 1582, 1480, 1455, 1434, 1186, 1158, 1096, 1060, 1027, 998, 854, 742, 705, 692, 522, 513, 428 cm^{-1}. Anal. Calcd for $C_{43}H_{37}ClP_2PtS$: C, 58.80; H, 4.25. Found: C, 58.64; H, 4.25.

***trans*-Pt(SC_6H_4-3-OMe)(Cl)(PPh_3)$_2$ (1c).** Yellow solid. mp: 192−193 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.95−7.90 (m, 12 H), 7.04−6.97 (m, 19 H), 6.75 (m, 1 H), 6.61 (t, J = 7.6 Hz, 1 H), 6.40 (d, J = 7.6 Hz, 1 H), 3.26 (s, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.6 (s, J_{Pt-P} = 2745 Hz). IR (KBr) 3462, 3048, 2988, 2830, 2354, 1581, 1480, 1467, 1435, 1310, 1276, 1239, 1218, 1183, 1097, 1071, 1046, 998, 857, 743, 706, 692, 540, 522, 513, 500 cm^{-1}. Anal. Calcd for $C_{43}H_{37}ClOP_2PtS$: C, 57.75; H, 4.17. Found: C, 57.97; H, 4.21.

***trans*-Pt(SC_6H_4-4-OMe)(Cl)(PPh_3)$_2$ (1d).** Yellow solid. mp: 214−216 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.94−7.91 (m, 12 H), 7.09 (d, J = 8.0 Hz, 2 H), 6.99−6.98 (m, 18 H), 6.31 (d, J = 8.4 Hz, 2 H), 3.25 (s, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.6 (s, J_{Pt-P} = 2773 Hz). IR (KBr): 3056, 2358, 2340, 1485, 1434, 1280, 1234, 1182, 1096, 1028, 826, 746, 693, 627, 580, 523, 511, 440 cm^{-1}. Anal. Calcd for $C_{43}H_{37}ClOP_2PtS$: C, 57.75; H, 4.17. Found: C, 57.68; H, 4.12.

***trans*-Pt(SC_6H_4-2-F)(Cl)(PPh_3)$_2$ (1e).** Yellow solid. mp: 211−212 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.00 (t, J = 8.8 Hz, 1 H), 7.92−7.84 (m, 12 H), 7.00−6.91 (m, 18 H), 6.55−6.51 (m, 1 H), 6.48−6.42 (m, 1 H), 6.29−6.24 (m, 1 H). ^{31}P NMR (160 MHz,

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C_6D_6): δ 24.5 (s, J_{Pt-P} = 2717 Hz). IR (KBr): 3054, 2350, 1957, 1587, 1558, 1480, 1460, 1435, 1310, 1250, 1210, 1185, 1159, 1096, 1070, 1028, 998, 870, 810, 742, 706, 691, 618, 596, 522, 513, 499, 458, 430 cm^{-1}. Anal. Calcd for $C_{42}H_{34}ClFP_2PtS$: C, 57.18; H, 3.88. Found: C, 58.20; H, 3.82.

***trans*-Pt(SC$_6$H$_4$-4-Cl)(Cl)(PPh$_3$)$_2$ (1f).** Yellow solid. mp: 219−220 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.89−7.84 (m, 12 H), 7.05 (d, J = 8.0 Hz, 2 H), 6.96−6.95 (m, 18 H), 6.61 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 134.3 (t, J = 6.0 Hz), 130.3 (s), 129.9 (s), 128.8 (t, J = 28.4 Hz), 127.7 (s), 127.2 (t, J = 5.5 Hz), 126.6 (s), 125.8 (s). ^{31}P NMR (160 MHz, C_6D_6): δ 24.3 (s, J_{Pt-P} = 2718 Hz). IR (KBr): 3422, 3049, 2356, 1618, 1570, 1480, 1468, 1434, 1306, 1184, 1092, 1028, 1008, 998, 818, 808, 752, 743, 704, 692, 540, 523, 512, 488, 418 cm^{-1}. Anal. Calcd for $C_{42}H_{34}Cl_2P_2PtS$: C, 56.13; H, 3.81. Found: C, 55.85; H, 3.81.

***trans*-Pt(SC$_6$H$_4$-3-Cl)(Cl)(PPh$_3$)$_2$ (1 g).** Yellow solid. mp: 217−218 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.91−7.86 (m, 12 H), 7.38 (m, 1 H), 7.01−6.97 (m, 18 H), 6.89−6.86 (m, 1 H), 6.65−6.62 (m, 1 H), 6.29 (t, J = 8.0 Hz, 1 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.4 (s, J_{Pt-P} = 2706 Hz). IR (KBr) 3494, 3056, 2361, 2341, 1652, 1571, 1480, 1450, 1436, 1392, 1308, 1182, 1098, 1074, 1028, 999, 856, 776, 742, 706, 691, 676, 638, 523, 513, 500 cm^{-1}. Anal. Calcd for $C_{42}H_{34}Cl_2P_2PtS$: C, 56.13; H, 3.81. Found: C, 55.94; H, 3.88.

***trans*-Pt(SC$_6$H$_4$-2-Cl)(Cl)(PPh$_3$)$_2$ (1h).** Yellow solid. mp: 212−214 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.26 (d, J = 7.6 Hz, 1 H), 7.89−7.87 (m, 12 H), 6.98−6.96 (m, 18 H), 6.71 (d, J = 7.6 Hz, 1 H), 6.61 (t, J = 7.2 Hz, 1 H), 6.41 (t, J = 7.6 Hz, 1 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.5 (s, J_{Pt-P} = 2715 Hz). IR (KBr) 3424, 3050, 1892, 1570, 1480, 1433, 1309, 1273, 1240, 1185, 1158, 1096, 1033, 998, 850, 740, 692, 660, 618, 540, 520, 452, 435, 417 cm^{-1}. Anal. Calcd for $C_{42}H_{34}Cl_2P_2PtS$: C, 56.13; H, 3.81. Found: C, 55.84; H, 3.75.

***trans*-Pt(SC$_6$H$_4$-4-Br)(Cl)(PPh$_3$)$_2$ (1i).** Yellow solid. mp: 209−210 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.88−7.83 (m, 12 H), 6.99 (d, J = 8.4 Hz, 2 H), 6.96−6.94 (m, 18 H), 6.74 (d, J = 8.4 Hz, 2 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.3 (s, J_{Pt-P} = 2714 Hz). IR (KBr): 3050, 1573, 1480, 1464, 1434, 1382, 1308, 1184, 1097, 1027, 1004, 844, 806, 752, 743, 704, 692, 540, 523, 512, 483, 462, 442 cm^{-1}. Anal. Calcd for $C_{42}H_{34}BrClP_2PtS$: C, 53.48; H, 3.63. Found: C, 54.04; H, 3.60.

***trans*-Pt(SC$_6$H$_4$-2-*i*-Pr)(Cl)(PPh$_3$)$_2$ (1j).** Yellow solid. mp: 196−197 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.47 (d, J = 7.2 Hz, 1 H), 7.92−7.87 (m, 12 H), 6.97−6.96 (m, 18 H), 6.82−6.74 (m, 2 H), 6.70−6.68 (m, 1 H), 2.98 (quint, J = 6.8 Hz, 1 H), 0.99 (d, J = 6.8 Hz, 6 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.5 (s, J_{Pt-P} = 2757 Hz). IR (KBr): 3436, 3048, 2951, 2860, 1580, 1481, 1480, 1461, 1434, 1358, 1310, 1274, 1186, 1158, 1096, 1071, 1051, 1029, 999, 840, 744, 730, 691, 618, 522, 512, 462, 431 cm^{-1}. Anal. Calcd for $C_{45}H_{41}ClP_2PtS$: C, 59.63; H, 4.56. Found: C, 59.42; H, 4.52.

***trans*-Pt(SC$_6$H$_4$-4-Me)(Cl)[P(C$_6$H$_4$-4-Me)$_3$]$_2$ (1k).** Yellow solid. mp: 215−217 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.94 (q, J = 5.6 Hz, 12 H), 7.30 (d, J = 8.0 Hz, 2 H), 6.88 (d, J = 7.6 Hz, 12 H), 6.54 (d, J = 8.0 Hz, 2 H), 2.04 (s, 3 H), 1.95 (s, 18 H). ^{31}P NMR (160 MHz, C_6D_6): δ 23.0 (s, J_{Pt-P} = 2734 Hz). IR (KBr): 3424, 3018, 2918, 2863, 1598, 1560, 1498, 1482, 1448, 1396, 1310, 1189, 1098, 1020, 799, 708, 644, 631, 612, 522, 478 cm^{-1}. Anal. Calcd for $C_{49}H_{49}ClP_2PtS$: C, 61.15; H, 5.13. Found: C, 60.98; H, 5.10.

***trans*-Pt(SC$_6$H$_4$-4-Me)(Cl)[P(C$_6$H$_4$-4-OMe)$_3$]$_2$ (1l).** Yellow solid. mp: 105−107 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.99−7.95 (m, 12 H), 7.42 (d, J = 8.0 Hz, 2 H), 6.68 (d, J = 8.0 Hz, 12 H), 6.57 (d, J = 7.6 Hz, 2 H), 3.17 (s, 18 H), 2.02 (s, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 21.1 (s, J_{Pt-P} = 2708 Hz). IR (KBr): 2930, 2835, 1594, 1570, 1500, 1483, 1460, 1440, 1404, 1289, 1253, 1180, 1100, 1029, 825, 800, 719, 648, 536, 507, 452, 433, cm^{-1}. Anal. Calcd for $C_{49}H_{49}ClO_6P_2PtS$: C, 55.60; H, 4.67. Found: C, 56.03; H, 4.68.

Table 1. Crystallographic Data for *trans*-**1i**

formula	$C_{43}H_{36}BrCl_3P_2PtS$
fw	1028.12
T (°C)	23.0
λ (Å)	0.71069
space group	$P\bar{1}$ (No. 2)
a (Å)	11.6513(5)
b (Å)	12.5267(8)
c (Å)	14.5392(8)
α (deg)	76.714(2)
β (deg)	88.574(2)
γ (deg)	79.061(3)
V (Å^3)	2027.3(2)
Z	2
D_{calcd} (g/cm^3)	1.684
μ (cm^{-1})	47.94
R indices [$I > 2\sigma(I)$][a]	
R1	0.0403
wR2	0.114

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

***trans*-Pt(SC$_6$H$_4$-4-Me)(Cl)[P(C$_6$H$_4$-4-CF$_3$)$_3$]$_2$ (1m).** Yellow solid. mp: 214−215 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.65−7.60 (m, 12 H), 7.23 (d, J = 8.0 Hz, 12 H), 6.80 (d, J = 8.4 Hz, 2 H), 6.42 (d, J = 8.4 Hz, 2 H), 1.99 (s, 3 H). ^{31}P NMR (160 MHz, C_6D_6): δ 24.0 (s, J_{Pt-P} = 2837 Hz). IR (KBr) 1610, 1486, 1398, 1325, 1170, 1129, 1063, 1017, 831, 808, 706, 599, 527, 444, 417 cm^{-1}. Anal. Calcd for $C_{49}H_{31}ClF_{18}P_2PtS$: C, 45.75; H, 2.43. Found: C, 45.82; H, 2.54.

X-ray Crystallography. The crystal was mounted on a glass capillary. Data collection was performed on a Rigaku RAXIS−RAPID Imaging Plate diffractometer (Mo Kα, λ = 0.71069 Å) with graphite-monochromated Mo Kα radiation. The structure was solved by heavy-atom Patterson methods, expanded using Fourier techniques, and refined with full-matrix least-squares. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. All calculations were performed by using the teXsan crystallographic software program package. A summary of the fundamental crystal data and experimental parameters for the structure determination of complex trans-**1i** is given in Table 1.

Synthesis of the Mixture of *cis*-1a and *cis*-4a. *cis*-PtCl$_2$(PPh$_3$)$_2$ (158 mg, 0.2 mmol), C_6H_6 (20 mL), and 5 N NaOH(aq) (0.12 mL) were added to a dry three-necked flask equipped with an additional flask. Then the C_6H_6 (2 mL) solution of PhSH (0.0224 g 0.2 mmol) was added gradually, and the resultant reaction mixture was stirred for a total of 30 min. Then the reaction mixture was filtered; hexane (100 mL) was added to the filtered solution, and the resultant solid was filtered, washed over methanol, ether, and hexane, and dried in vacuo to yield a solid (35 mg) containing *cis*-**1a** and *cis*-**4a** in a ratio of 36/64.

Reaction of *cis*-1a-Containing 4a with Bases (Table 3). *cis*-**1a**-containing **4a** (4.0 mg, 0.0016 mmol of *cis*-**1a** and 0.0028 mmol of *cis*-**4a**), S=P(C$_6$H$_4$-4-Me)$_3$ (1.7 mg, 0.0051 mmol as an internal standard), C_6D_6 (0.5 mL), and pyridine (0.9 mg, 0.010 mmol) were mixed in a Pyrex NMR tube. The ^{31}P NMR spectrum taken after 20 min showed complete isomerization of *cis*-**1a** to *trans*-**1a**. The reactions using other additives shown in Table 2 were carried out and monitored by NMR spectroscopy in a similar manner.

Synthesis of Authentic *cis*-4a. *cis*-PtCl$_2$(PPh$_3$)$_2$ (316 mg, 0.40 mmol) and toluene (25 mL) were added in a dry three-necked flask equipped with an additional flask. Then the ether (8 mL) solution of PhSH (97 mg, 0.88 mmol) and NEt$_3$ (178 mg, 1.76 mmol) was

Table 2. Reaction of **2a** with **3a** in the Presence of Base[a]

$PtCl_2(PPh_3)_2$ (**2a**) + PhSH (**3a**) $\xrightarrow{\text{base}}$ $PtCl(SPh)(PPh_3)_2$ (**1a**) + $Pt(SPh)_2(PPh_3)_2$ (**4a**)

run	**2a**	base	**1a** (%)[b] (cis/trans)	**4a** (%)[b] (cis/trans)
1	cis	Et_3N	8 (100/0)	55 (100/0)
2	trans	Et_3N	13 (0/100)	38 (76/24)
3[c]	cis	Et_3N	7 (0/100)	44 (100/0)
4[d]	cis	KOH	30 (93/7)	38 (100/0)
5[d]	cis	NaOH	34 (94/6)	36 (100/0)
6	cis	pyridine	93 (0/100)	6 (0/100)
7	trans	pyridine	93 (0/100)	7 (0/100)
8[e]	cis	pyridine	71[f] (0/100)	–
9[g]	cis	pyridine	81 (34/66)	8 (100/0)

[a] Unless otherwise noted, **2a** (0.010 mmol), **3a** (0.012 mmol), $S{=}P(C_6H_4\text{-}4\text{-}Me)_3$ (internal standard) and base (0.05 mmol) in C_6D_6 (0.5 mL) at 25 °C for 1 h. [b] Yields were tentatively determined from $^{31}P\{^1H\}$ NMR spectra. [c] PPh_3 (0.05 mmol). [d] Aqueous 5 N. [e] 0.40 mmol scale. [f] Isolated yield. [g] In CD_2Cl_2 (0.5 mL).

added gradually, and the resultant reaction mixture was stirred for a total of 6 h. Then the solvent was removed by evaporation, and the yellow residue was dissolved in 20 mL of CH_2Cl_2. This solution was extracted with 200 mL of water and dried over anhydrous $MgSO_4$. After the solvent was removed by evaporation, the resultant solid was recrystallized from CH_2Cl_2/ether to give *cis*-**4a** as a yellow solid (227 mg, 60%).

Isomerization of *cis*-4a into *trans*-4a. 4a (5.1 mg, 0.0054 mmol), $S{=}P(C_6H_4\text{-}4\text{-}Me)_3$ (2.6 mg, 0.0077 mmol as an internal standard), and C_6D_6 (0.5 mL) were mixed in a Pyrex NMR tube. The ^{31}P NMR spectrum taken after 42 h showed that the ratio of *cis*-**4a**/*trans*-**4a** was 96/4.

***cis*-4a.** ^{31}P NMR (160 MHz, C_6D_6): δ 23.8 (s, $J_{Pt-P} = 2880$ Hz).

***trans*-4a.** ^{31}P NMR (160 MHz, C_6D_6): δ 23.4 (s, $J_{Pt-P} = 2823$ Hz).

Solubility of *cis*-2a in C_6D_6. Because of the low solubility of *cis*-**2a**, the sample containing *cis*-**2a** (6.7 mg, 0.0085 mmol) and $S{=}P(C_6H_4\text{-}4\text{-}Me)_3$ (2.7 mg, 0.0080 mmol as an internal standard) in C_6D_6 (0.5 mL) was accumulated for 12 h by ^{31}P NMR spectroscopy at 25 °C. Thus, the solubility of *cis*-**2a** was calculated to be ca. 1.6×10^{-4} mmol in 0.5 mL of C_6D_6.

Dimerization of 4b into 4b′. 4b (5.0 mg, 0.0050 mmol), $S{=}P(C_6H_4\text{-}4\text{-}Me)_3$ (1.7 mg, 0.0050 mmol as an internal standard), and C_6D_6 (0.5 mL) were combined in a Pyrex NMR tube. The solution was heated at 60 °C, and the reaction was monitored by ^{31}P NMR spectra. The spectrum taken after 6 h showed the ratio of **4b**/$[Pt(SC_6H_4\text{-}4\text{-}OMe)_2(PPh_3)]_2$ (**4b′**) was 51/49.

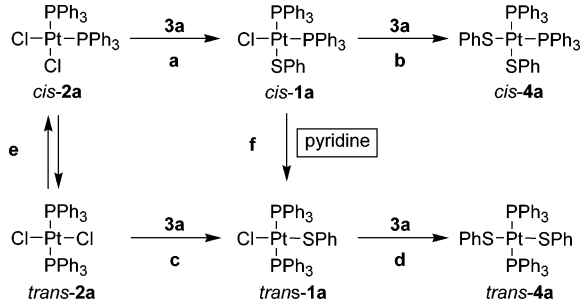
4b. ^{31}P NMR (160 MHz, C_6D_6): δ 23.3 (s, $J_{Pt-P} = 2889$ Hz).

4b′ (syn/anti mixture). ^{31}P NMR (160 MHz, C_6D_6): δ 21.1 (s, $J_{Pt-P} = 3398$ Hz), 19.9 (s, $J_{Pt-P} = 3367$ Hz).

Results and Discussion

First, the reactions of $Pt(Cl)_2(PPh_3)_2$ (**2a**) with PhSH (**3a**) (1.2 equiv) in the presence of some bases (5 equiv) were monitored by ^{31}P NMR spectra (Table 2). When the reaction of *cis*-**2** with **3a** was carried out using Et_3N as a base in C_6D_6 (0.5 mL), *cis*-$Pt(SPh)(Cl)(PPh_3)_2$ (**1a**) and *cis*-$Pt(SPh)_2(PPh_3)_2$ (**4a**) were obtained in 8 and 55% (92% based on **3a**) yields, respectively after 1 h (run 1).[13] Given that the solubility of *cis*-**2a** is significantly low (1.6×10^{-4} mmol in 0.5 mL of C_6D_6 at 25 °C), this result indicated that **3a** dominantly reacted with in situ generated *cis*-**1a**, whose

Scheme 1. Possible Reaction Routes for the Reaction of **2a** with **3a**



solubility is much higher than that of *cis*-**2a** to produce *cis*-**4a** as a major product (through path a and b in Scheme 1). On the other hand, when *trans*-**2a** was employed instead of *cis*-**2a**, 13% of *trans*-**1a** and 38% of **4a** (cis/trans = 76/24) were produced (run 2).[14] Among these three complexes, the formation of *trans*-**1a** and *trans*-**4a** can be accounted for by the stereoselective substitution of ArS for the Cl atom of *trans*-**2a** and *trans*-**1a** (through path c and d in Scheme 1). Because *trans*-**2a** isomerizes into *cis*-**2a** in solution[15] and the *trans*-effect of PPh_3 is stronger than that of Cl,[16] the formation of *cis*-**4a** through the paths e, a, and then b would become the major route. No yield improvement was achieved in the presence of 5 equiv of PPh_3 (run 3), even though the fact that no formation of *cis*-**1a** was confirmed suggested that PPh_3 somewhat catalyzed the isomerization of *cis*-**1a** to *trans*-**1a** (vide infra). While the yields of **1a** slightly increased when KOH (aq) and NaOH (aq) were employed as bases, a considerable amount of **4a** was produced as a byproduct in both cases (runs 4 and 5). In stark contrast, a dramatic change occurred when pyridine was selected. Both reactions employing *cis*-**2a** and *trans*-**2a** produced *trans*-**1a** highly selectively in 93% yields (runs 6 and 7). This can be reasonably explained by the assumption that the the isomerization of *cis*-**1a** into *trans*-**1a** (path f in Scheme 1) is facilely promoted by the presence of pyridine. That is, when *cis*-**2a** was employed as a starting complex, the kinetic product *cis*-**1a** generated through path a was converted into *trans*-**1a**, whose reactivity toward **3a** (path d) is significantly lower than that of *cis*-**2a** because of the weaker *trans*-effect of SAr than that of PPh_3 of *cis*-**2a**.[16] On the other hand, when *trans*-**2a** was employed, as predicted by the result of the reaction using Et_3N as a base (run 2), *cis*-**2a** can be generated via path e and would react with **3a** to produce *cis*-**1a**. However, if *cis*-**1a** was rapidly isomerized to *trans*-**1a** by the effect of pyridine, again, *trans*-**1a** is selectively produced. Complex **1a** was isolated in a 71% yield from the preparative scale of the reaction after purification by PTLC (run 8). The choice

(14) *trans*-**4a** is thermodynamically more stable than *cis*-**4a**; however, isomerization from *cis*-**4a** to *trans*-**4a** was very sluggish in C_6D_6 (cis/trans = 96/4 from *cis*-**4a** at 25 °C after 42 h).

(15) When *trans*-**2a**, whose purity was checked in $CDCl_3$ with a ^{31}P NMR spectrum, was dissolved in C_6D_6, a mixture of **2a** with cis/trans = 10/90 was detected in solution. (a) Redfield, D. A.; Nelson, J. H. *Inorg. Chem.* **1973**, *12*, 15. (b) Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278.

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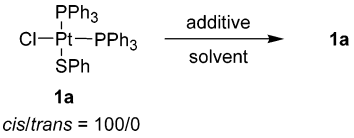
Table 3. cis-to-trans Isomerization of **1a** in the Presence of Additives[a]

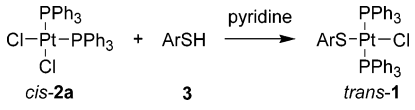


cis/*trans* = 100/0

run	solvent	additive	time	cis/trans
1	C_6D_6	pyridine	20 min	0/100
2	C_6D_6	none	1 h	100/0
3	C_6D_6	NEt_3	1 h	100/0
4	C_6D_6	PPh_3	20 min	57/43
5	CD_2Cl_2	pyridine	20 min	90/10

[a] *cis*-**1a** (0.0016 mmol containing 0.0028 mmol of *cis*-**4a**) and additive (0.01 mmol) in solvent (0.5 mL).

Table 4. Syntheses of **1** with Various Functional Groups[a]



run	**3**	Ar	**1**	yield (%)[b]
1	**3b**	C_6H_4-2-Me	**1b**	55
2	**3c**	C_6H_4-3-OMe	**1c**	88
3	**3d**	C_6H_4-4-OMe	**1d**	49
4	**3e**	C_6H_4-2-F	**1e**	59
5[c]	**3f**	C_6H_4-4-Cl	**1f**	66
6	**3 g**	C_6H_4-3-Cl	**1g**	87
7[d]	**3h**	C_6H_4-2-Cl	**1h**	58
8	**3i**	C_6H_4-4-Br	**1i**	80
9	**3j**	C_6H_4-2-*i*-Pr	**1j**	57

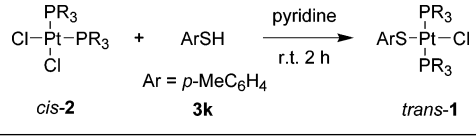
[a] *cis*-**2a** (0.40 mmol), **3** (0.42 mmol), and pyridine (2.0 mmol) in C_6H_6 (20 mL) at 25 °C for 2 h. [b] Isolated yield after PTLC. [c] A mixture of *trans*-**1f**/*trans*-**4f** = 98/2 was obtained as a crude reaction mixture. [d] A mixture of *trans*-**1h**/*cis*-**2a**/*trans*-**4h** = 92/4/4 was obtained as a crude mixture.

of solvent is also crucial for the selective formation of *trans*-**1a**. The reaction of *cis*-**2a** with **3a** using pyridine as a base performed in CD_2Cl_2 yielded a mixture of **1a** (81%, cis/trans = 34/66) and *cis*-**4a** (8%) (run 9).

The *cis*-**1a**-containing *cis*-**4a** prepared by reprecipitation from the reaction mixture using NaOH as a base (run 5 in Table 2) was subjected to a solution of pyridine (run 1 in Table 3) to obtain more conclusive evidence for the cis-to-trans isomerization by pyridine. As expected, complete isomerization into *trans*-**1a** was confirmed after 20 min at 25 °C. On the other hand, in the absence of base or in the presence of Et_3N, no isomerization took place after 1 h (runs 2 and 3). It must be noted that PPh_3, which is generally considered to be a good catalyst for the cis-to-trans isomerization of transition-metal complexes showed much inferior activity (cis/trans = 57/43, run 4). Furthermore, in accordance with the data of run 9 in Table 2, the isomerization was very sluggish in CD_2Cl_2 even in the presence of pyridine (run 5). Although the role of pyridine in C_6D_6 was not cleared at the moment, pyridine, which is much less bulky than PPh_3 and shows stronger affinity for the Pt(II) complex than NEt_3, would coordinate to vacant coordination site of *cis*-**1** and facilitate the isomerization.[11a]

The generality of the present method for the syntheses of **1** by the reactions of *cis*-**2** with **3** is shown in Tables 4 and 5. *trans*-**1** platinum complexes with various substituents such as Me, OMe, F, Cl, Br, and *i*-Pr in Ar were all successfully

Table 5. Syntheses of **1** with Various Phosphine Ligands[a]



run	*cis*-**2**	PR_3	*trans*-**1**	yield (%)[b]
1	**2b**	$P(C_6H_4$-4-Me$)_3$	**1k**	53
2[c]	**2c**	$P(C_6H_4$-4-OMe$)_3$	**1l**	37
3	**2d**	$P(C_6H_4$-4-$CF_3)_3$	**1m**	80
4	**2e**	$PMePh_2$	**1n**	35[d]
5	**2f**	$P(OEt)_3$	**1o**	—[e]

[a] *cis*-**2** (0.40 mmol), **3k** (0.42 mmol), and pyridine (2.0 mmol) in C_6H_6 (20 mL) at 25 °C for 2 h. [b] Isolated yield after PTLC. [c] A mixture of *trans*-**1l**/*cis*-**2c**/*trans*-**4l** = 87/4/9 was obtained as a crude reaction mixture. [d] NMR yield. [e] Complicated mixture.

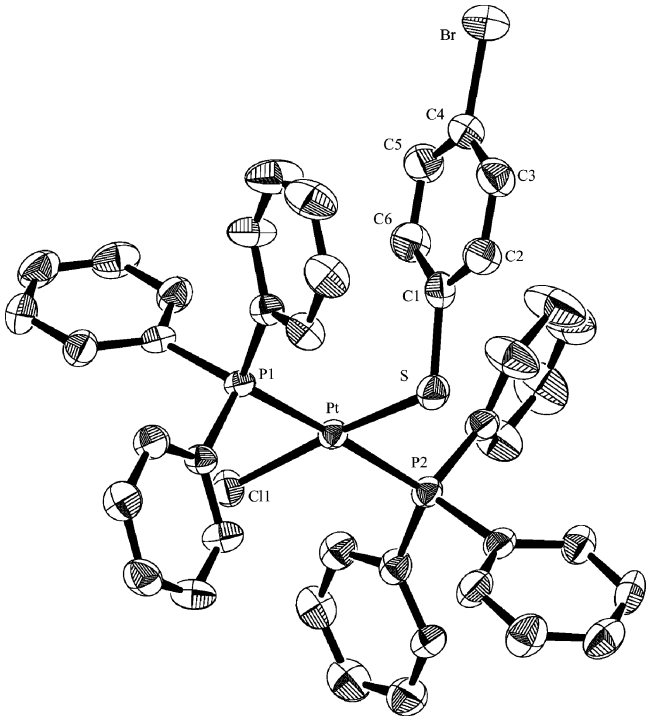


Figure 1. Molecular structure of *trans*-**1i** (thermal ellipsoids set at 50% probability). Solvent molecule (CH_2Cl_2) omitted for clarity.

isolated in moderate to good yields (runs 1−9; 49−88% in Table 4) using the present protocol. Crystals of **1i** (Ar = C_6H_4-4-Br) suitable for X-ray crystallographic analyses were obtained from a CH_2Cl_2/hexane solution, and its ORTEP diagram is shown in Figure 1. The present method was also applicable to platinum complexes with moieties other than PPh_3. The corresponding **1** complexes with $P(C_6H_4$-4-Me$)_3$, $P(C_6H_4$-4-OMe$)_3$, and $P(C_6H_4$-4-$CF_3)_3$ as ligands were also synthesized and successfully isolated in 53, 37, and 80% yields, respectively (runs 1−3 in Table 5). The reaction using *cis*-$PtCl_2(PMePh_2)_2$ (*cis*-**2e**) formed the desired product *trans*-$Pt(SAr)(Cl)(PMePh_2)_2$ (*trans*-**1n**), albeit in a low yield (run 4), while the reaction of *cis*-$Pt(Cl)_2[P(OEt)_3]_2$ (*cis*-**2f**) with **3k** gave a complicated mixture (run 5).

Although the vulnerability of complex **1** to disproportionation and polymerization[8,10] was implicated in the papers dealing with the preparation of platinum complexes with an S−Pt−Cl fragment,[9] all **1** complexes prepared by the present

methodology were actually quite stable in C_6D_6 solution even at 60 °C for 6 h. On the other hand, dithiolate complex *trans*-$Pt(SC_6H_4\text{-}4\text{-}OMe)_2(PPh_3)_2$ (**4b**) was converted into a mixture of **4b** and its dimeric form, $[Pt(SC_6H_4\text{-}4\text{-}OMe)_2(PPh_3)]_2$ (**4b′**), in a ratio of 51/49 under the same conditions. This fact can be rationalized by assuming that the high electronegativity of the *trans*-Cl ligand made a significant contribution toward preventing dimerization and polymerization by decreasing the basicity of the lone pairs on SAr group.[8]

Conclusion

In conclusion, the general synthetic procedure of *trans*-$Pt(SAr)(Cl)(PAr'_3)_2$ has been established by taking advantage of pyridine as a cis-to-trans isomerization catalyst. This study also indicated that the participation of pyridine not only as a base but also as an isomerization catalyst must be taken into consideration when thinking about the reaction mechanisms of some catalytic reactions such as Heck and Sonogashira reactions.[17] The utility of **1** for the examination of the insertion of unsaturated molecules into the S−Pt bond is now under investigation.

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for elemental analysis.

Supporting Information Available: X-ray crystallographic data file (CIF) for *trans*-**1i**, ^{1}H and ^{31}P NMR spectra of *trans*-**1e**, *trans*-**1i**, and *trans*-**1l**, and ^{31}P NMR spectra of crude reaction mixtures of run 5 and run 7 in Table 4 and run 2 in Table 5. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051780L

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