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Preparation of Tethered Palladium Catalysis Supported on Gold(111) and Its Surface Characterization by X-ray Photoelectron Spectroscopy (XPS)

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Chelated tethering ligands were confined on a Au(111) substrate, and the confinement of the ligands was confirmed by X-ray photoelectron spectroscopy (XPS). Palladium was anchored to the ligands to construct heterogeneous {Pd}–L–Au(111) catalysts (L = ligand). A {Pd}–Au(111) catalyst was also prepared by adsorbing the Pd complex directly on the Au(111) substrate without a tethering ligand. Both types of catalysts were used in the Mizoroki–Heck reaction to evaluate their catalytic activities. The tether-ligated Pd catalyst {Pd}–L–Au(111) activity decreased with recycling, whereas the {Pd}–Au(111) catalyst was quite stable upon reuse. The surfaces of both catalyst types were evaluated using XPS to determine the presence of tethering ligands and/or Pd on the Au(111). The ligands of the tether-ligated Pd catalysts could not be detected on the Au(111) surface after the Mizoroki–Heck reaction, which suggests weak bonding of the S–Au by which the ligand is bound to the Au(111) substrate.

The development of efficient methods to facilitate the recovery and reuse of organometallic catalysts is an important goal in catalytic organic chemistry. Organopalladium catalysts are widely used to yield a wide variety of organic compounds.[1] The Pd-catalyzed Mizoroki–Heck reaction[2] has received considerable attention as it offers a versatile method for carbon–carbon bond formation.[3] For this reaction to be industrially feasible, it is particularly important to reduce both the loss and presence of Pd catalysts in the product solution due to the expense and toxicity. Heterogeneous catalysis is a promising option for solving these problems and a variety of heterogeneous Pd catalysts have been developed.[4] Polymer- or silica-supported tether ligands containing P, S, or nitrogen-containing heterocyclic carbene (NHC) donor centers are well-defined candidates for the construction of heterogeneous Pd catalysts and they have been used as recyclable catalysts for cross-coupling reactions.[5] Recently, we reported the development of novel heterogeneous Pd catalysts supported on a sulfur-terminated semiconductor GaAs(001) and evaluated their catalytic activities in cross-coupling reactions.[6] This catalyst was easily recovered and handled in aerobic conditions, and exhibited high activity and stability during recycling in the Mizoroki–Heck reaction.[6d] However, its surface is complicated due to the existence of several S and Pd species and it was rather difficult to know the actual active species of this catalyst. On the other hand, immobilization of molecular catalyst onto crystalline Si(111) surface has also been used to the surface-attached polymerizaton.[6e] Tethered palladium catalyst onto crystalline silicon, Si(111)–BOX–Pd, has been reported as a recyclable catalyst in the aerobic oxidation of benzylic alcohols.[6f] These findings prompted us to construct the much more simplified heterogeneous catalyst by anchoring the Pd to the metal substrate functionalized with P-, S-, or N-containing chelating tethering ligands.

Gold is a fascinating metal substrate for the adsorption of organic molecules due to the fact that it does not form a surface oxide under atmospheric conditions and its surface is satisfactorily inert to many chemicals, but it easily chemisorbs thiols (RSH), disulfides (RSSR), and dialkylsulfides (RSR), which spontaneously organize into self-assembled monolayers, and it has thus been investigated extensively in recent years.[7,8] The self-assembled monolayers of functionalized tether molecules on gold are capable of undergoing chemical reactions under mild conditions.[9] Some transition-metal complexes tethered on gold powder are also catalytically active.[10] However, as far as we know, experiments to know the strength of S–Au bonding have not been reported.

In the present study, we attempted to confine the P, S, or NHC donor center-containing chelating tethering ligands on Au(111) film. These ligand-modified Au(111) films were reacted with Pd sources to prepare tethered Pd complexes supported on Au(111) substrate and then applied to the Mizoroki–Heck reaction to evaluate their catalytic activity. The existence of the tether ligands on the gold surface was also examined by X-ray photoelectron spectroscopy (XPS).

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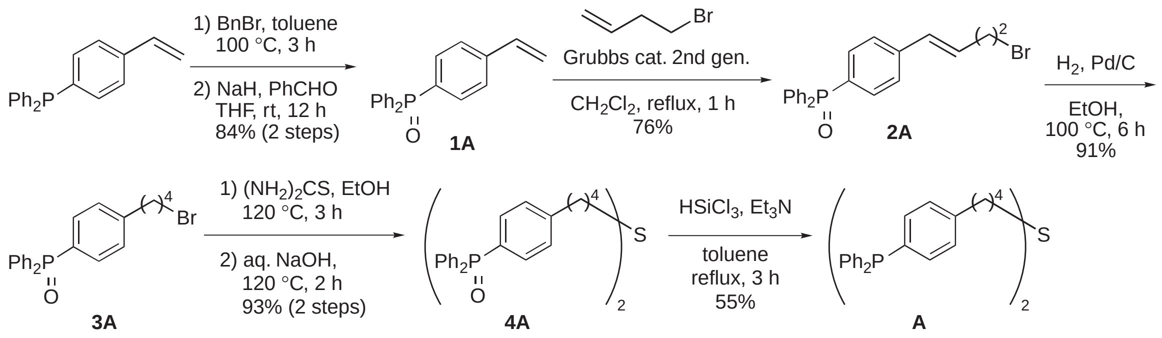
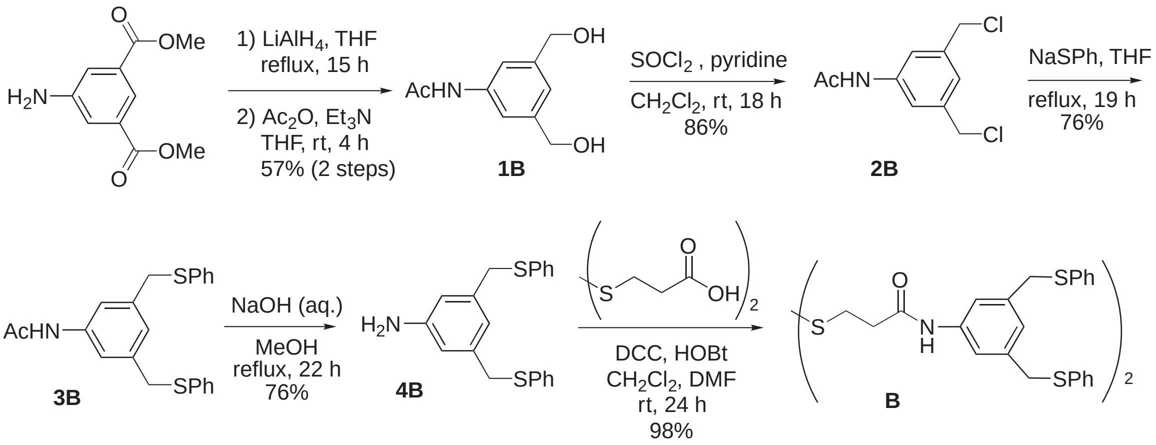
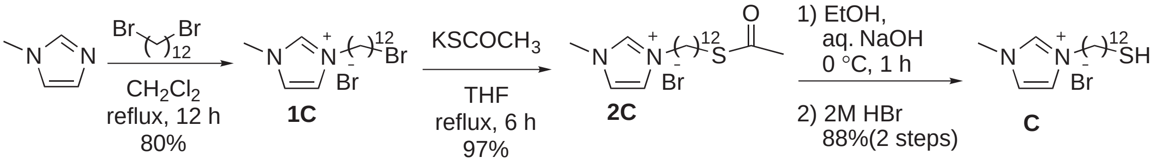


Scheme 1. Synthesis of ligand **A**.



Scheme 2. Synthesis of ligand **B**.



Scheme 3. Synthesis of ligand **C**.

Results and Discussion

Preparation of Tethering Ligands and Adsorption of Ligands on Au(111) Substrate. The tethering ligands containing P, S, and NHC donor centers were synthesized according to Schemes 1, 2, and 3, respectively, and are referred to as ligand **A**, **B**, and **C**, respectively. The ligands were allowed to adsorb onto the Au(111) substrate to prepare ligand-modified Au(111) film (L–Au(111)) and then reacted with the Pd source to obtain the expected catalysts {Pd}–L–Au(111).

Au(111) film deposited on a mica support was used as the substrate for adsorption of the ligands. The Au(111) plate was used as purchased or cleaned with piranha solution prior to use for ligand adsorption. We prepared the Au(111) film modified with ligand **A** [L(**A**)–Au(111)] by immersing the Au(111) plate in 1 mmol dm^{-3} ligand **A** solution in $CHCl_3$ at 60 °C for 12 h in Ar atmosphere. The plate was removed from the solution and rinsed with $CHCl_3$ and then dried under a stream of Ar gas. Thereafter, the plate was kept in a glovebox to avoid the oxidation of P. The Au(111) film modified with ligand **B** [L(**B**)–Au(111)] was prepared by immersing the Au(111) plate in 1 mmol dm^{-3} ligand **B** solution in chloroform–methanol (19:1) at 50 °C for 12 h.[8b] The plate was removed from the solution and rinsed with the same solvent mixture and dried under a stream of Ar gas. The Au(111) film modified with ligand **C** [L(**C**)–Au(111)] was prepared by immersing the Au(111) plate in 1 mmol dm^{-3} thiol-terminated ligand **C** solution in absolute ethanol at room temperature for 3 h.[11] The plate was removed from the solution and rinsed with ethanol and dried under a stream of Ar gas. These ligand-modified Au(111) films [L–Au(111)] were examined by XPS.

Surface Characterization by XPS 1. The surface of the L–Au(111) films was characterized by XPS (Figure 1). Spectra a, b, c, and d correspond to L(**A**)–Au(111), L(**B**)–Au(111), L(**C**)–Au(111), and pure Au(111) films, respectively. A clear peak due to C 1s was observed in spectra a, b, and c, which suggests the presence of organic molecules on the Au(111) surface. Characteristic peaks due to P, S, or N atoms were considered as the evidence of ligand confinement on the Au(111) surface. The peak due to P for ligand **A** was not detected in

Table 1. Catalytic Activities of the {Pd}–L(**C**)–Au(111) and {Pd}–Au(111) Catalysts in the Mizoroki–Heck Reaction

Entry	Catalyst	Pd adsorption	Yield/%[a)										
			1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	mean
1	$\mathbf{C_1}$	$Pd(OAc)_2$, THF, 50 °C, 4 h	100	75	73	68	69	51	79	61	75	58	71
2	$\mathbf{C_1}$	$Pd(OAc)_2$, THF, 50 °C, 4 h	12	6	—	—	—	—	—	—	—	—	9[b)
3	$\mathbf{C_1}$	$Pd(OAc)_2$, THF, 50 °C, 4 h	82	47	37	20	22	15	19	23	—	—	33[c)
4	$\mathbf{C_2}$	$Pd(OAc)_2$, THF, 80 °C, 4 h	93	35	29	58	37	27	28	32	35	37	41
5	$\mathbf{C_3}$	$Pd(OAc)_2$, THF, 50 °C, 12 h	73	87	93	72	56	49	59	34	32	30	59
6	$\mathbf{C_4}$	$Pd(OAc)_2$, THF, 80 °C, 12 h	61	81	98	99	89	99	87	86	89	67	86
7	**W**[d)	$Pd(dba)_2$, xylene, 85 °C, 4 h	100	100	100	100	100	100	94	79	87	83	94

a) Yields were determined by NMR analysis. b) The Mizoroki–Heck reaction was performed at 50 °C and the average yield of two runs is shown. c) The Mizoroki–Heck reaction was performed at 80 °C and the average yield of eight runs is shown. d) Pd was directly adsorbed onto the Au(111) substrate without a tethering ligand.

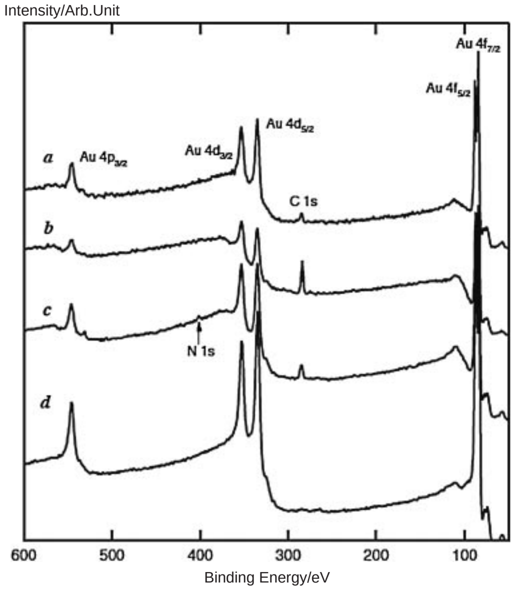
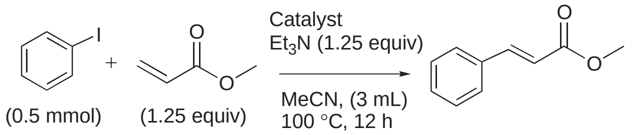


Figure 1. XPS spectra for the ligand-modified gold surface. Spectra a, b, c, and d correspond to L(**A**)–Au(111), L(**B**)–Au(111), L(**C**)–Au(111), and pure Au(111), respectively.

spectrum a of the L(**A**)–Au(111) film. Although very weak peaks at around 229 eV (S 2s) and 165 eV (S 2p) due to S were observed in spectrum b, no peak due to N was detected for the Au(111) film modified with ligand **B**. On the other hand, a clear peak due to N 1s was observed at around 402 eV in spectrum c for the L(**C**)–Au(111) film. Notably, the N 1s peak for L(**C**)–Au(111) was observed when the Au(111) film was used without prior piranha treatment or after treatment with piranha for 1 min or 1 h (some spectra not shown). Intense peaks due to Au were observed for all three ligand-modified Au(111) films. The presence of the Au peak does not necessarily indicate a bare gold surface. Possible reasons for an intense Au signal are as follows: The ligands covered the surface completely but the layer was thin enough to allow photoelectrons to penetrate through the film; or the ligands covered the surface partially and the Au atoms were exposed. Based on the clear N 1s peak, the above XPS results suggest that ligand **C** was surely bound to the gold surface, whereas the results were ambiguous for ligands **A** and **B**. The L(**C**)–Au(111) film was then applied for preparation of the Pd catalysts.



Scheme 4. Mizoroki–Heck reaction.

Preparation of Pd Catalysts. Based on the above results, the adsorbed imidazolium ligand **C** was converted to a carbene-type ligand in the glovebox by treating the L(**C**)–Au(111) film with potassium *tert*-butoxide (^{t}BuOK) in THF[12] and then Pd was anchored by immersing the film in a solution of $Pd(OAc)_2$ in THF. The prepared catalyst, hereafter called {Pd}–L(**C**)–Au(111), was rinsed with MeCN and dried under a stream of Ar gas. Pd catalyst supported on Au(111), {Pd}–Au(111), was also prepared by the direct adsorption of $Pd(dba)_2$ in xylene.

Catalytic Activity. The catalytic activities of the {Pd}–L(**C**)–Au(111) and {Pd}–Au(111) catalysts in the Mizoroki–Heck reaction of iodobenzene and methyl acrylate as a model reaction were examined (Scheme 4). At the end of reaction, the catalyst was removed from the reaction mixture and rinsed several times with MeCN. The reaction mixture was concentrated in vacuo to obtain a residue. The yield of methyl *trans*-cinnamate, which is the desired product of the reaction, was determined by ^{1}H NMR spectroscopy. The recovered catalyst was subjected to another reaction as a second run and this procedure was repeated at least 10 times to evaluate the stability of the catalyst. The catalytic activities for each run are shown in Table 1.

The catalytic activities of the {Pd}–L(**C**)–Au(111) catalysts depended on the Pd adsorption step as well as the Mizoroki–Heck reaction temperature. Catalyst $\mathbf{C_1}$ prepared by Pd adsorption at 50 °C for 4 h gave a 71% average yield from 10 successive Mizoroki–Heck reactions at 100 °C (Entry 1). The yield was considerably lower, however, for $\mathbf{C_1}$ at a lower reaction temperature (Entries 2 and 3). Increasing the Pd adsorption temperature did not promote the catalytic activities. Catalyst $\mathbf{C_2}$ prepared by Pd adsorption at 80 °C gave a 41% average yield (Entry 4). The activities of both catalysts $\mathbf{C_1}$ and $\mathbf{C_2}$ decreased considerably after the second run. On the other hand, catalysts $\mathbf{C_3}$ and $\mathbf{C_4}$, prepared by increasing the Pd adsorption time, had increased activity at first and then decreased activity (Entries 5 and 6). The surface characteristics of these catalysts

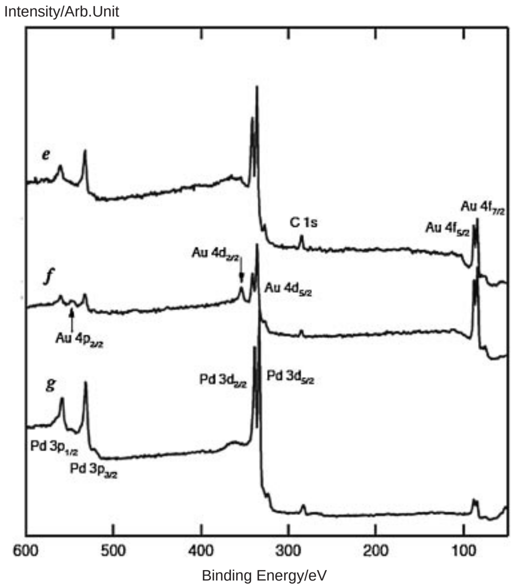


Figure 2. XPS spectra of catalysts {Pd}–L(**C**)–Au(111) and {Pd}–Au(111). Spectra e and f correspond to catalyst $\mathbf{C}_1$ before and after application to the Mizoroki–Heck reaction, respectively, and spectrum g corresponds to catalyst **W** after application to the Mizoroki–Heck reaction.

observed by XPS measurements will be useful for understanding these activities.

Catalyst {Pd}–Au(111) (Entry 7), prepared by the direct adsorption of $Pd(dba)_2$ on the Au(111) substrate without a tether, had the best performance among the catalysts. The activity slightly decreased after the 7th run, but it had an impressive 94% average yield for 10 successive runs.

Surface Characterization by XPS 2. XPS was used to evaluate the fate of the ligands and the state of the Pd after the Mizoroki–Heck reaction. The XPS results for {Pd}–L(**C**)–Au(111) (catalyst $\mathbf{C}_1$) and {Pd}–Au(111) (catalyst **W**) are shown in Figure 2. Spectra e and f are for the catalyst $\mathbf{C}_1$ before and after application to the Mizoroki–Heck reaction, respectively, and spectrum g is for catalyst **W** after application to the Mizoroki–Heck reaction. Clear peaks of Pd 3d core-level photoemission were observed for all catalysts, indicating that Pd was definitely immobilized to the surface. No peak due to the N of ligand **C** was observed for catalyst {Pd}–L(**C**)–Au(111) either before or after the Mizoroki–Heck reaction. The absence of a peak due to N 1s for {Pd}–L(**C**)–Au(111) was surprising, because the peak was clearly observed for L(**C**)–Au(111). One possibility is that the S–Au bond by which the ligands are bound to the gold surface was too weak to survive the Mizoroki–Heck reaction conditions or even the Pd adsorption step. It is also possible that the peaks could not be detected due to the low signal intensity and the presence of immobilized Pd on top of the ligand. Similar results were reported for the sulfur-terminated {Pd}–S–GaAs catalyst in which S 2p photoemission peaks could not be detected by XPS and was ascribed due to the immobilization of Pd on top of the S.[6c]

The results shown in Table 1 demonstrate that the catalytic activity for catalyst {Pd}–L(**C**)–Au(111) was mainly dependent on the Pd adsorption step. The drastic decrease in catalytic activity after the second run (Entries 1–4) suggested that the S–Au bonds were cleaved during the Mizoroki–Heck reaction and the tethered Pd complexes were washed away during the first run. The increase in catalytic activities of the catalyst prepared with a longer Pd adsorption time, however, suggests the adsorption of excess nontethered Pd, which may possess lower catalytic activity. After desorption of nontethered Pd, the catalytic activity increased. This may indirectly suggest the coverage of the tether ligand by excess Pd. If this is the case, then the absence of a ligand for catalyst $\mathbf{C}_1$ before applied to Mizoroki–Heck reaction according to the XPS measurements (spectrum e in Figure 2) is not surprising.

Although our previously reported catalyst {Pd}–S–GaAs was stable enough to survive the Mizoroki–Heck reaction, the mechanistic approach appeared to be simpler for the tethered Pd catalyst, {Pd}–L(**C**)–Au(111). Since the catalytic Pd center is far away from the metal support in {Pd}–L(**C**)–Au(111) catalyst, the reaction can proceed like a homogeneous reaction. In this approach, however, varieties of tethering ligands can be adsorbed on the Au(111) substrate to make highly functionalized catalyst. These are not possible in {Pd}–S–GaAs catalyst in which the Pd is directly adsorbed to the sulfur-terminated GaAs(001). The surface inertness of Au(111) also makes it a better candidate as a solid substrate compared to GaAs(001) surface which oxidizes upon atmospheric condition.[6a]

Conclusion

The original goal of this investigation was to evaluate the feasibility of using solid-supported tethering ligands to construct heterogeneous tether-ligated Pd catalysts. We attempted to confine the functionalized tether ligands on a gold surface through S–Au bonding and then Pd was anchored to the ligands. To the best of our knowledge, this is the first report of XPS analysis the S–Au bonds are not strong enough to maintain the ligands on the gold substrate under the standard Mizoroki–Heck reaction. We previously reported that sulfur-termination of GaAs(001) is essential for the preparation of stable Pd catalysts and the resultant catalyst {Pd}–S–GaAs is reusable in the Mizoroki–Heck reaction many times without the loss of catalytic activity.[6b,6d] The present report, thus, indicates that the S–GaAs bond is stronger than the S–Au bond. These studies, however, demonstrated that the transition-metal catalysts tethered on a gold substrate may be appropriate for mild reaction conditions. The results also demonstrated that it is possible to form effective catalysts by adsorbing the Pd complexes directly onto the Au surface and it can be used in high-temperature reactions. The catalysts are easy to recover and transferred under aerobic conditions using a pair of tweezers.

Experimental

General. All moisture-sensitive reactions were performed under an Ar atmosphere unless cited. Solvents were dried using molecular sieves. Reagents were obtained from commercial sources and were used without further purification. Mica-supported Au(111) film plate was purchased from Agilent and was cleaned with piranha solution prior to use in some cases. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 400 MHz, with TMS as an internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 100 MHz. ^{31}P NMR spectra were recorded at 25 °C unless otherwise noted at 161 MHz, with 80% H_3PO_4 (δ 0) as an external standard. XPS measurement was carried out using Mg Kα radiation (K.E. = 1253 eV) and Al Kα radiation (K.E. = 1487 eV). The energy shift due to sample charging was corrected by using Au 4f$_{7/2}$ (84.0 eV) as an internal standard. Syntheses of air-unstable chemicals were carried out in a glovebox (Miwa, DBO-1NKP-TA) containing less than 1 ppm of oxygen and water. Flash column chromatographies were performed with silica gel 60 N (spherical, neutral, 40–50 µm, Kanto Chemical Co., Inc.).

Synthesis of Tethering Ligand A and Adsorption of Ligand on Au(111) Substrate. The ligand **A** was synthesized in six steps as described in Scheme 1. The details for the synthesis of ligand **A** and the adsorption of ligand **A** on Au(111) substrate are given below.

Synthesis of Diphenyl(4-vinylphenyl)phosphine Oxide (1A): A mixture of diphenyl(4-vinylphenyl)phosphine (490 mg, 1.7 mmol) and benzyl bromide (0.23 mL, 1.9 mmol) in toluene (10.0 mL) was stirred at 100 °C for 3 h under Ar atmosphere. After cooling to rt, the precipitate was filtered and washed with cool toluene and then dried under vacuum to get (bromobenzyl)diphenyl(4-vinylphenyl)phosphonium salt (700 mg, 1.5 mmol) as a white solid. The resulting salt was mixed with NaH (68.0 mg, 60% in oil, 1.7 mmol) and benzaldehyde (0.17 mL, 1.7 mmol) and then THF (8.0 mL) was added. The resulting mixture was stirred at rt for 12 h and then quenched with saturated aq NH_4Cl. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, and then dried over Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexane:EtOAc = 20:1, then 1:1) to afford **1A** (436 mg, 84% for 2 steps) as a viscous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 (1H, d, $J = 10.8$ Hz), 5.85 (1H, d, $J = 17.6$ Hz), 6.74 (1H, dd, $J = 10.8$, 17.6 Hz), 7.46–7.70 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.5, 126.1, 126.2, 128.4, 128.5, 131.0, 131.9, 131.9, 131.9, 132.0, 132.0, 132.3, 132.4, 133.0, 135.8, 135.8, 140.9, 140.9; ^{31}P NMR (100 MHz, $CDCl_3$): δ 29.3; IR (neat): ν 3054, 2967, 1598, 1436, 1395, 1182, 1115 cm^{-1}; LRMS (EI) m/z 303 $(M-H)^+$; HRMS (FAB) calcd for $C_{20}H_{18}O_1P_1$ 305.1095 $(M+H)^+$, found 305.1077.

Synthesis of {4-[(*E*)-4-Bromo-1-butenyl]phenyl}diphenylphosphine Oxide (2A): To a solution of **1A** (183 mg, 0.60 mmol) in CH_2Cl_2 (8.0 mL) was added Grubbs catalyst second generation (5.8 mg, 0.69×10^{-2} mmol) and 4-bromo-1-butene (0.1 mL, 1.0 mmol). The resulting mixture was refluxed at 50 °C for 1 h under Ar atmosphere. After cooling to rt, the solvent was removed in vacuo and then purified by column chromatography on silica gel (hexane:EtOAc = 20:1, then 1:2) to afford **2A** (189 mg, 76%) as a viscous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 (2H, dt, $J = 6.8$, 6.8 Hz), 3.48 (2H, t, $J = 6.8$ Hz), 6.30 (1H, dt, $J = 16.0$, 6.8 Hz), 7.43–7.69 (15H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.8, 36.0, 126.0, 126.1, 128.3, 128.4, 129.5, 130.5, 131.6, 131.6, 131.6, 131.8, 131.8, 131.9, 132.0, 132.3, 132.4, 133.0, 140.4, 140.4 (overlapped); IR (neat): ν 3430, 3054, 2960, 1597, 1436, 1181, 1115, 967 cm^{-1}; LRMS (EI) m/z 409 $(M-H)^+$; HRMS (FAB) calcd for $C_{22}H_{21}Br_1O_1P_1$ 411.0513 $(M+H)^+$, found 411.0496.

Synthesis of [4-(4-Bromobutyl)phenyl]diphenylphosphine Oxide (3A): To a solution of **2A** (100 mg, 0.25 mmol) in EtOH (7.0 mL) was added Pd/C (26.0 mg, 10% wt). The resulting mixture was refluxed at 100 °C for 6 h under H_2 atmosphere. After cooling to rt, the mixture was filtered through a Celite pad. The filtrate was concentrated in vacuo and then purified by column chromatography on silica gel (hexane:EtOAc = 1:2) to afford **3A** (91 mg, 91%) as a viscous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75–1.92 (4H, m), 2.69 (2H, t, $J = 7.6$ Hz), 3.41 (2H, t, $J = 6.4$ Hz), 7.26–7.69 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.4, 32.1, 33.3, 34.9, 128.4, 128.5, 128.6, 130.4, 131.8, 131.9, 132.1, 132.2, 132.2, 146.1, 146.2 (overlapped); ^{31}P NMR (100 MHz, $CDCl_3$): δ 29.7; IR (neat): ν 3447, 3053, 2930, 2856, 1600, 1436, 1182, 1116 cm^{-1}; LRMS (EI) m/z 411 $(M-H)^+$; HRMS (FAB) calcd for $C_{22}H_{23}Br_1O_1P_1$ 413.0652 $(M+H)^+$, found 413.0660.

Synthesis of Bis[4-(4-diphenylphosphinoyl)butyl] Sulfide (4A): To a solution of **3A** (32.0 mg, 0.077 mmol) in EtOH (7.0 mL) was added thiourea (6.0 mg, 0.077 mmol). The resulting mixture was refluxed at 120 °C for 3 h and then aq NaOH (5 mg, 0.11 mmol in 1.5 mL H_2O) was added and refluxed again at 120 °C for 2 h. After cooling to rt, the reaction mixture was quenched with H_2SO_4 and extracted with ether. The organic layer was dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and then purified by column chromatography on silica gel (EtOAc:MeOH = 5:1) to afford **4A** (26.0 mg, 93%) as a viscous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (4H, tt, $J = 7.2$, 7.2 Hz), 1.72 (4H, tt, $J = 7.2$, 7.2 Hz), 2.50 (4H, t, $J = 7.2$ Hz), 2.66 (4H, t, $J = 7.2$ Hz), 7.25–7.69 (28H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.9, 30.0, 31.7, 35.3, 128.2, 128.3, 128.4, 128.5, 128.9, 129.9, 131.7, 131.7, 131.8, 131.9, 132.0, 132.0, 132.1, 133.0, 146.5, 146.5 (overlapped); ^{31}P NMR (100 MHz, $CDCl_3$): δ 29.6; IR (neat): ν 3054, 2929, 2854, 1601, 1436, 1184, 1116 cm^{-1}; LRMS (FAB) m/z 699 $(M+H)^+$; HRMS (FAB) calcd for $C_{44}H_{45}O_2P_2S$ 699.2616 $(M+H)^+$, found 699.2585.

Synthesis of Bis[4-(4-diphenylphosphino)butyl] Sulfide (Ligand A): To a solution of **4A** (56.0 mg, 0.15 mmol) in toluene (7.0 mL) was added Et_3N (0.070 mL, 0.66 mmol) and trichlorosilane (0.070 mL, 0.64 mmol). The resulting mixture was refluxed at 130 °C for 3 h under Ar atmosphere and then 30 wt % aq NaOH (10.0 mL) was added and stirred at 60 °C for 1 h. After cooling down the reaction mixture to rt, 5.0 mL of H_2O was added and extracted with toluene (15.0 mL × 3). The organic layer was washed with brine and then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and then purified by flash column chromatography on silica gel (hexane:EtOAc = 20:1, and then hexane:$CHCl_3$ = 4:1 using PTLC) to afford ligand **A** (31 mg, 55%) as a viscous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56–1.74 (8H, m), 2.49 (4H, t, $J = 7.2$ Hz), 2.61 (4H, t, $J = 7.2$ Hz), 7.13–7.33 (28H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.2, 30.3, 31.9, 35.3, 128.4, 128.4, 128.5, 128.6, 128.6, 128.7, 132.0, 132.1, 133.5, 133.7, 133.8, 133.9, 134.0, 137.4, 137.5, 143.0 (overlapped); ^{31}P NMR (100 MHz, $CDCl_3$): δ −5.8; IR (neat): ν 3067, 3051, 3013, 2923, 2853, 1597, 1584, 1477, 1432, 1090, 741, 693 cm^{-1}; LRMS (FAB) m/z 667 $(M+H)^+$; HRMS (FAB) calcd for $C_{44}H_{45}P_2S$ 667.2717 $(M+H)^+$, found 667.2673.

Adsorption of Ligand A on Au(111) Substrate: The Au(111) plates either cleaned with piranha solution (a mixture of concd H_2SO_4 and 30% H_2O_2 in 3:1 ratio) or without cleaning, both types were used for adsorption of ligands. In piranha treatment, the Au(111) plate was immersed in piranha solution for 1 min and rinsed exhaustively with distilled, deionized water and absolute ethanol and then dried with a stream of Ar gas. The clean Au(111) plate was immersed in 1 mM solution of ligand

A in $CHCl_3$ at 60 °C for 12 h under an Ar atmosphere. The ligand-modified Au(111) plate was rinsed with $CHCl_3$ and then dried under a stream of Ar gas and kept in glovebox.

Synthesis of Tethering Ligand B and Adsorption of Ligand on Au(111) Substrate. The ligand **B** was synthesized in six steps as described in Scheme 2. Species **1B**, **2B**, **3B**, and **4B** were synthesized according to a previously reported procedure.[5g] The details for the synthesis of ligand **B** from species **4B** and the adsorption of ligand **B** on Au(111) substrate are given below.

Synthesis of *N*,*N*′-3,5-Bis[(phenylthio)methyl]phenyl-3,3′-dithiopropanamide (Ligand B): To a solution of 3,3′-dithiodipropionic acid (21 mg, 0.10 mmol) in CH_2Cl_2 (2.0 mL) and DMF (0.1 mL) was added HOBt (28 mg, 0.21 mmol). The mixture was stirred at rt for 15 min, and then added DCC (43 mg, 0.21 mmol) and 3,5-bis(phenylthiomethyl)aniline (**4B**) (71 mg, 0.21 mmol). The solution was stirred at rt for 24 h, and then filtered through a Celite pad. The filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane: EtOAc = 3:1) to afford ligand **B** (83 mg, 98% with respect to 3,3′-dithiodipropionic acid) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (t, $J = 6.8$ Hz, 4H), 3.05 (t, $J = 6.6$ Hz, 4H), 3.97 (s, 8H), 6.96 (s, 2H), 7.14–7.26 (m, 20H), 7.40 (s, 4H), 7.71 (s, 2H); LRMS (EI) m/z 849 $(M - H)^+$.

Adsorption of Ligand B on Au(111) Substrate: The Au(111) plate was immersed in 1 mM solution of ligand **B** in $CHCl_3$:MeOH = 19:1 at 50 °C for 12 h under an Ar atmosphere. The ligand-modified Au(111) plate was rinsed with the same solvent mixture at 50 °C and then dried under a stream of Ar gas.

Synthesis of Tethering Ligand C and Adsorption of Ligand on Au(111) Substrate. The synthesis of thiol-terminated ligand **C** and the adsorption of ligand **C** onto the Au(111) substrate were carried out according to the published method to obtain the ligand-modified Au(111) film L(**C**)–Au(111).[11]

Preparation of {Pd}–L(C)–Au(111) Catalysts: Experiment was carried out in glovebox. To a solution of ^{t}BuOK (1.0 mg) in THF (3.00 mL) was immersed the ligand-modified Au(111) film L(**C**)–Au(111) and stirred gently at rt for 20 min.[12] The plate was rinsed with THF and then immersed in a solution of $Pd(OAc)_2$ (4.0 mg) in THF (3.00 mL). The solution was stirred gently at 50 °C for 4 h. Catalyst was also prepared for longer adsorption period as well as changing the temperature. After cooling to rt, plate was rinsed with MeCN and dried under a stream of Ar gas to get the catalyst {Pd}–L(**C**)–Au(111).

Preparation of {Pd}–Au(111) Catalyst. The Au(111) plate was immersed in a solution of $Pd(dba)_2$ (10.0 mg) in xylene (3.00 mL) and stirred gently at 85 °C for 4 h. The plate was then rinsed with MeCN and dried under stream of Ar gas to get the catalyst {Pd}–Au(111).

General Procedure for the Mizoroki–Heck Reaction. A mixture of iodobenzene (56.0 µL, 0.500 mmol), methyl methacrylate (56.2 µL, 0.625 mmol), and Et_3N (87.1 µL, 0.625 mmol) in MeCN (3.00 mL) was heated in the presence of catalyst at 100 °C (bath temperature) for 12 h under an argon atmosphere without stirring. After the reaction mixture was cooled to rt, the catalyst was removed and rinsed several times with MeCN. The yield of methyl *trans*-cinnamate was determined by ^{1}H NMR analysis (0.250 mmol, 25.6 µL of nitrobenzene was initially added to the reaction mixture as an internal standard). The yield was calculated from the integrated ratio of the starting material iodobenzene and methyl *trans*-cinnamate.[6d] The recovered catalyst was again subjected to the above reaction conditions as a second run. The procedure was repeated more than 10 runs.

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References

1 a) E. Negishi, *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley Interscience, New York, **2002**. b) J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, New York, **2004**.

2 a) T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. b) R. F. Heck, J. P. Nolley, Jr., *J. Org. Chem.* **1972**, *37*, 2320. c) K. Mori, T. Mizoroki, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1505. d) R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146.

3 a) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009. b) A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A: Chem.* **2001**, *173*, 249.

4 a) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133. b) N. T. S. Phan, M. V. D. Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609.

5 a) D. E. Bergbreiter, P. L. Osburn, Y.-S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531. b) J. H. Clark, D. J. Macquarrie, E. B. Mubofu, *Green Chem.* **2000**, *2*, 53. c) M. Lagasi, P. Moggi, *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 61. d) R. Chanthateyanonth, H. Alper, *J. Mol. Catal. A: Chem.* **2003**, *201*, 23. e) Y. M. A. Yamada, K. Takeda, H. Takahashi, S. Ikegami, *Tetrahedron* **2004**, *60*, 4097. f) K. Yu, W. Sommer, M. Weck, C. W. Jones, *J. Catal.* **2004**, *226*, 101. g) K. Yu, W. Sommer, J. M. Richardson, M. Weck, C. W. Jones, *Adv. Synth. Catal.* **2005**, *347*, 161. h) Ö. Aksin, H. Türkmen, L. Artok, B. Çetinkaya, C. Ni, O. Büyükgüngör, E. Özkal, *J. Organomet. Chem.* **2006**, *691*, 3027. i) B. Altava, M. I. Burguete, E. García-Verdugo, N. Karbass, S. V. Luis, A. Puzary, V. Sans, *Tetrahedron Lett.* **2006**, *47*, 2311. j) M. Shokouhimehr, J.-H. Kim, Y.-S. Lee, *Synlett* **2006**, 618.

6 a) M. Arisawa, S. Tsukamoto, M. Shimoda, M. Pristovsek, A. Nishida, *Jpn. J. Appl. Phys.* **2002**, *41*, L1197. b) I. Takamiya, S. Tsukamoto, M. Shimoda, N. Miyashita, M. Arisawa, Y. Arakawa, A. Nishida, *Chem. Lett.* **2004**, *33*, 1208. c) I. Takamiya, S. Tsukamoto, M. Shimoda, M. Arisawa, A. Nishida, Y. Arakawa, *Jpn. J. Appl. Phys.* **2006**, *45*, L475. d) M. Arisawa, M. Hamada, I. Takamiya, M. Shimoda, S. Tsukamoto, Y. Arakawa, A. Nishida, *Adv. Synth. Catal.* **2006**, *348*, 1063. Immobilization of a molecular catalyst onto crystalline silicon has also been reported: e) A. Juang, O. A. Scherman, R. H. Grubbs, N. S. Lewis, *Langmuir* **2001**, *17*, 1321. f) K. Hara, S. Tayama, H. Kano, T. Masuda, S. Takakusagi, T. Kondo, K. Uosaki, M. Sawamura, *Chem. Commun.* **2007**, 4280.

7 a) A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir—Blodgett to Self-Assembly*, Academic Press, New York, **1991**. b) P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh, R. G. Nuzzo, *J. Am. Chem. Soc.* **1991**, *113*, 7152. c) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.

8 a) C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **1989**, *111*, 321. b) P. Wagner, M. Hegner, H.-J. Güntherodt, G. Semenza, *Langmuir*

1995, *11*, 3867. c) H. Takiguchi, K. Sato, T. Ishida, K. Abe, K. Yase, K. Tamada, *Langmuir* **2000**, *16*, 1703. d) J. Noh, T. Murase, K. Nakajima, H. Lee, M. Hara, *J. Phys. Chem. B* **2000**, *104*, 7411. e) H.-J. v. Manen, T. Auletta, B. Dordi, H. Schönherr, G. J. Vancso, F. C. J. M. v. Veggel, D. N. Reinhoudt, *Adv. Funct. Mater.* **2002**, *12*, 811.

9 a) K. Motesharei, D. C. Myles, *J. Am. Chem. Soc.* **1997**, *119*, 6674. b) H. H. J. Persson, W. R. Caseri, U. W. Suter, *Langmuir* **2001**, *17*, 3643.

10 a) M. Bartz, J. Küther, R. Seshadri, W. Tremel, *Angew. Chem., Int. Ed.* **1998**, *37*, 2466. b) H. Li, Y.-Y. Luk, M. Mrksich, *Langmuir* **1999**, *15*, 4957. c) H. Gao, R. J. Angelici, *Can. J. Chem.* **2001**, *79*, 578. d) K. Marubayashi, S. Takizawa, T. Kawakusu, T. Arai, H. Sasai, *Org. Lett.* **2003**, *5*, 4409. e) T. Belser, M. Stöhr, A. Pfaltz, *J. Am. Chem. Soc.* **2005**, *127*, 8720.

11 B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong, S.-G. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 480.

12 A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523.