

Activation of Aromatic Carbon–Hydrogen Bonds by Palladium(II) Acetate–Dialkyl Sulfide Systems. Formation and Characterization of Novel Diphenyltripalladium(II) Complexes

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Palladium(II) acetate reacts with benzene in the presence of dialkyl sulfides at 70 °C to afford novel diphenyltripalladium(II) complexes of $[(R^1SR^2)PhPd(\mu-MeCO_2)_2Pd(\mu-MeCO_2)_2PdPh(R^1SR^2)]$ (**1a**; $R^1=Bu^t$, $R^2=CH_2Bu^t$; **1b**; $R^1=R^2=Bu^t$; **1c**; $R^1=R^2=Pr^i$; **1d**; $R^1=R^2=Et$). Adducts, $[Pd(MeCO_2)_2(Bu^tSCH_2Bu^t)_2]$ and $[Pd(MeCO_2)_2(SPr^i)_2]$, prepared by the reactions of palladium(II) acetate and the corresponding dialkyl sulfides in benzene at 5–10 °C, change to **1a** and **1c**, respectively, on heating in benzene at 70 °C. In contrast, reactions of palladium(II) acetate with toluene or thiophene in the presence of diisopropyl sulfide afford no isolable tolyl- or thienyl-palladium species, but coupling products, i.e. bitolyls or bithienyls, are detected by GLC analysis. Treatment of **1b** with styrene produces *trans*-stilbene, whereas **1c** reacts with carbon monoxide as well as carbon dioxide to yield benzoic acid. When palladium(II) acetate and *t*-butyl phenethyl sulfide are heated at 80 °C in benzene, an adduct $[Pd(MeCO_2)_2(Bu^tSCH_2CH_2Ph)_2]$ is formed, in sharp contrast with the case of benzyl *t*-butyl sulfide, which gives a cyclopalladated complex under the same reaction conditions.

Although the metallations of arenes with non-transition metal compounds such as thallium¹⁾ and mercury compounds²⁾ are well-known, the activation of arene C–H bonds by transition metals is a subject undergoing current research in organometallic chemistry. Up to date, mainly two types of the preparations of σ -aryl complexes directly from arenes and transition metal compounds have been reported. The first type is the oxidative addition of arene C–H bonds to coordinatively unsaturated species which are photochemically generated from dihydridometal complexes such as $[W(\eta^5-C_5H_5)_2H_2]$ ³⁾ and $[M(\eta^5-C_5Me_5)H_2(PMe_3)]$ ($M=Rh$,⁴⁾ Ir ⁵⁾) or thermally generated from $[M(2-naphthyl)H(Me_2PCH_2CH_2PMe_2)_2]$ ($M=Fe$, Ru).⁶⁾ The second type is electrophilic substitution of arenes by metal complexes such as $AuCl_3$,⁷⁾ H_2PtCl_6 ,⁸⁾ and $[Rh(octaethylporphyrinato)Cl]-Ag$ salt.⁹⁾

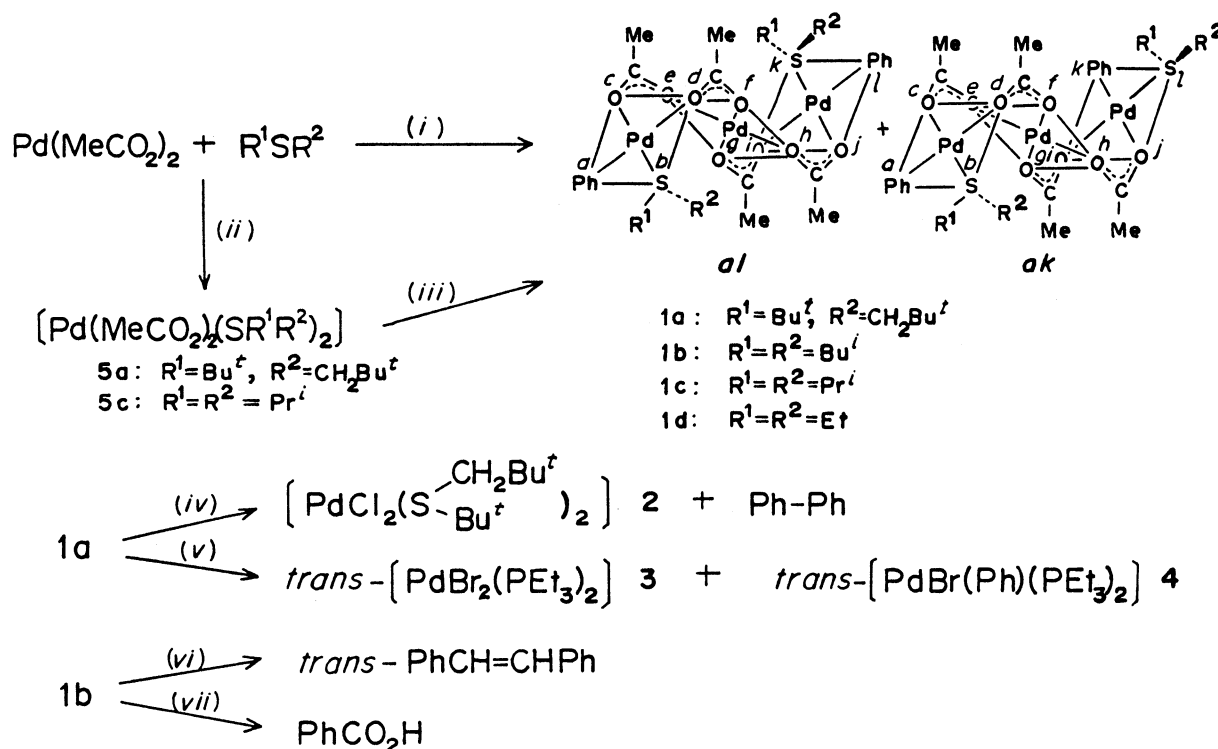
It was proposed that σ -aryl palladium(II) complexes were formed in the arylation of olefins,¹⁰⁾ or carbonylation¹¹⁾ and carboxylation¹²⁾ of arenes by palladium(II) acetate, but such the complex had never been isolated. Previously, we reported preliminary results about novel diphenyltripalladium(II) complexes isolated from palladium(II) acetate–dialkyl sulfide systems in benzene.¹³⁾ Here, we wish to report both the details of the C–H bond activation of arenes by the same systems and by a few additional ones and characterization of the resulting diphenyltripalladium(II) complexes.

Results and Discussion

Reactions of Palladium(II) Acetate with Dialkyl Sulfides in Benzene. Palladium(II) acetate reacted with *t*-butyl neopentyl sulfide in benzene at 70 °C to give yellow-brown crystals of **1a** and biphenyl (70% yield). The IR spectrum of **1a** showed newly a $\nu(C-H)$

frequency of the aromatic ring at 3040 cm^{-1} , together with the bands due to bridging acetato ligands at 1570, 1555, 1410, and 1395 cm^{-1} . The NMR data (¹H and ¹³C; see below) of **1a** in C_6D_6 confirmed the presence of phenyl groups as well as acetato and *t*-butyl neopentyl sulfide ligands. The molecular weight was determined to be 1055 by osmometry in benzene at 42 °C (Calcd for $C_{38}H_{62}O_8Pd_3S_2$: M , 1030.28). On the basis of these results and elemental analysis, **1a** was assigned as diphenyltripalladium(II) complex with four μ -acetato ligands, $[(Bu^tSCH_2Bu^t)PhPd(\mu-MeCO_2)_2Pd(\mu-MeCO_2)_2PdPh(Bu^tSCH_2Bu^t)]$. The ¹H NMR spectrum of **1a** exhibited the phenyl proton signals at δ 8.14 (d), 8.05 (d), and 6.95–7.5 (m). In addition, the acetato-methyl protons appeared as four singlets at δ 1.63 (3H), 1.73 (3H), 1.84 (3H), and 1.93 (3H), whereas the methyl protons of the sulfide moieties resonated as three singlets at δ 1.31 (18H, CH_2CMe_3), 1.39 (9H, $SCMe_3$), and 1.46 (9H, $SCMe_3$). These data indicated that **1a** consisted of two geometrical isomers, *al*- and *ak*-diphenyl types (Scheme 1) in a population ratio of 1:1. In the ¹³C{¹H} NMR spectrum,¹⁴⁾ signals due to the two isomers were observed almost separately.

Complex **1a** reacted with lithium chloride in acetone to give an adduct $[PdCl_2(Bu^tSCH_2Bu^t)_2]$ (**2**) but not a phenylpalladium species. However, biphenyl was detected in 70% yield based on **1a** by GLC analysis of the reaction mixture. In contrast, when **1a** was treated with triethylphosphine and lithium bromide in acetone, both *trans*- $[PdBr_2(PEt_3)_2]$ (**3**) and *trans*- $[PdBr(Ph)(PEt_3)_2]$ (**4**) were isolated in 61% and 14% yields, respectively. These results confirmed that **1a** contained phenylpalladium moieties as well as 'Pd(MeCO₂)₂' moiety. The formation of trinuclear palladium(II) complexes containing four μ -acetato ligands has been found in $[Pd_3(\eta^3-allyl)_2(\mu-MeCO_2)_4]$,¹⁵⁾



Scheme 1. Reactions of palladium(II) acetate with dialkyl sulfides in benzene and the reactivities of complexes **1a** and **1b**. (i) Benzene, 70°C. (ii) Benzene, 5–10°C. (iii) Benzene, 70°C. (iv) LiCl. (v) PEt_3 , LiBr. (vi) PhCH=CH_2 . (vii) CO or CO_2 .

Table 1. Yields, Melting Points, IR, and Analytical Data of the Complexes

Complex	Yield %	Mp ^{a)} θ _m /°C	IR/cm ⁻¹		Found (Calcd)(%)	
			ν(CH aromatic)	ν(COO)	C	H
1a	29 45 ^{b)}	139	3040	1570, 1555 1410, 1395	43.62(44.30)	5.94(6.07)
1b	37	152	3030	1570, 1550 1415, 1390	42.81(43.14)	5.81(5.83)
1c	27 29 ^{c)}	140	3020	1570, 1550 1400, 1375	40.67(40.62)	5.34(5.33)
1d	9	141	3030	1580, 1550 1410, 1375	37.32(37.77)	4.66(4.76)
2	41	205	—	—	42.94(43.42)	8.08(8.10)
3	61	135	—	—	28.38(28.68)	6.04(6.02)
4	19	104	3030	—	42.96(43.26)	6.92(7.06)
5a	19	128	—	1620, 1300	48.40(48.47)	8.39(8.50)
5c	53	108	—	1610, 1275	41.27(41.69)	7.50(7.43)
7	20	123	3060 3030	1620, 1300	54.96(54.85)	6.74(6.90)

a) With decomposition. b) Yield from **5a**. c) Yield from **5c**.

$[\text{Pd}_3(\text{CH}_2\text{CMe}_2\text{CH}_2\text{NMe}_2)_2(\mu\text{-MeCO}_2)_4]$,¹⁶⁾ and $[\text{Pd}_3(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2(\mu\text{-MeCO}_2)_4]$,¹⁷⁾ which were produced by the reactions of palladium(II) acetate with monoolefins, *N,N*-dimethylnepentylamine, and *N,N*-dimethyl-*o*-toluidine, respectively.

It is also found that when palladium(II) acetate was treated with benzene at 70°C for 2 h in the presence of each of diisobutyl, diisopropyl, and diethyl sulfides, the corresponding diphenyltripalladium(II) complexes $[(\text{R}^1\text{SR}^2)\text{PhPd}(\mu\text{-MeCO}_2)_2\text{Pd}(\mu\text{-MeCO}_2)_2\text{PdPh}(\text{R}^1\text{SR}^2)]$ (**1b**, $\text{R}^1 = \text{R}^2 = \text{Bu}^i$; **1c**, $\text{R}^1 = \text{R}^2 = \text{Pr}^i$; **1d**, $\text{R}^1 = \text{R}^2 = \text{Et}$) were

obtained with the formation of biphenyl in 12, 22, and 39% yields, respectively. The complexes **1b**–**1d** were characterized by means of elemental analyses (Table 1) and spectroscopic data (Tables 1 and 2). Complexes **1b**–**1d** were also composed of two isomers *al*- and *ak*-diphenyl types in population ratios of about 1:0.8.

Complexes **1a**–**1d** were fairly stable in solid state, but decomposed gradually in solution to give metallic palladium. Any good single crystal suitable for X-ray structural analysis could not be obtained owing to their instability in solution. It should be noted that

Table 2. ¹H NMR Data of the Complexes^{a)}

Complex	CH ₃	CH ₂	CH	CH ₃ COO	Aromatic
1a ^{b)}	1.31s 1.39s, 1.46s	3.5br	—	1.63s, 1.74s 1.84s, 1.93s	8.14d, ^{c)} 8.05d ^{c)} 7.3m
1b ^{b)}	0.87d ^{c)}	2.78d ^{d)} 2.86d ^{d)}	2.03n ^{d)}	1.66s, 1.78s 1.80s, 1.92s	7.94d ^{c)} 7.1m
1c ^{b)}	1.30d ^{d)} 1.49d ^{d)}	—	3.22h ^{d)}	1.62s 1.69s 1.79s, 1.86s	7.97d ^{c)} 7.05m
1d ^{b)}	1.15br	2.65br	—	1.59s, 1.75s 1.96s	8.08d, ^{c)} 8.16d ^{c)} 7.1m
2	1.14s, 1.41s	2.8br	—	—	—
3	1.06q ^{e)}	2.01 ^{f)}	—	—	—
4	1.07q ^{e)}	1.58 ^{f)}	—	—	6.89t, ^{e)} 6.97t ^{e)} 7.21d ^{e)}
5a	1.24s, 1.49s	2.35br	—	1.89s	—
5c	1.57d ^{g)}	—	3.04h ^{g)}	1.87s	—
7	1.55s	2.6br 3.4br	—	1.94s	7.3m

a) δ value in CDCl₃, unless noted elsewhere: s=singlet, d=doublet, t=triplet, q=quintet,

h=heptet, n=nonet, m=multiplet, br=broad. b) In C₆D₆. c) ³J_{HH}=8 Hz. d) ³J_{HH}=6 Hz.

e) ³J_{HH}=8 Hz. ³⁺⁵J_{PH}=8 Hz. f) Triple quartet with intensity ratio of 1:2:4:6:6:6:4:2:1.

³J_{HH}=8 Hz. ²⁺⁴J_{PH}=4 Hz. g) ³J_{HH}=7 Hz.

the benzene molecule was directly activated by palladium(II) acetate in the presence of dialkyl sulfides to give the diphenyltripalladium(II) complexes of **1a**—**1d**.

When di-*t*-butyl sulfide or tetrahydrothiophene was heated in benzene at 70 °C for 2 h with palladium(II) acetate, the corresponding diphenyltripalladium(II) complex like **1** could not be isolated in both cases. However, biphenyl was detected in 19% (in the case of SBut₂) and 40% yields [in the case of S(CH₂)₄] based on palladium(II) acetate by GLC analysis of the reaction mixtures. When palladium(II) acetate was treated with benzene at 70 °C for 2 h in the absence of dialkyl sulfide, no biphenyl was detected. Taking these facts into consideration, it seemed likely that benzene was also activated in the cases of di-*t*-butyl sulfide and tetrahydrothiophene.

The reactions of palladium(II) acetate with *t*-butyl neopentyl sulfide and diisopropyl sulfide, carried out in benzene at 5–10 °C, produced mononuclear addition complexes, [Pd(MeCO₂)₂(Bu^tSCH₂Bu^t)] (**5a**) and [Pd(MeCO₂)₂(SPri₂)₂] (**5c**), respectively. Complex **5a** was heated in benzene at 70 °C for 2 h to give yellow-brown crystals, which was ascribed to the diphenyltripalladium(II) complex **1a**, but not to a binuclear palladium(II) species such as [(Bu^tSCH₂Bu^t)PhPd(μ-MeCO₂)₂PdPh(Bu^tSCH₂Bu^t)]. Similarly, **5c** was converted to **1c** under the same conditions.

Reactivity of the Diphenyltripalladium(II) Complex [(Bu₂S)PhPd(μ-MeCO₂)₂Pd(μ-MeCO₂)₂PdPh(SBu₂)] (1b**).** The complex **1b** reacted with styrene in THF at room temperature to produce *trans*-stilbene in 94% yield. When carbon monoxide was bubbled through a THF solution of **1b** at room temperature and the reaction mixture was treated with sodium hydrogencarbonate and hydrochloric acid, benzoic acid was obtained

in 64% yield by GLC analysis. Benzoic acid was also produced in 9% yield (GLC analysis) by treating **1b** with 4.4×10⁶ Pa of carbon dioxide in a THF-MeCO₂H (4:1) mixed solvent in an autoclave at 60 °C. Furthermore, very small amount of phenol was obtained by treating **1b** with pressurized mixture of dioxygen and carbon monoxide.¹⁸⁾

It was reported that benzene was carbonylated with carbon monoxide (1.52×10⁶ Pa) and was also carboxylated with carbon dioxide (3.04×10⁶ Pa) in the presence of palladium(II) acetate to give benzoic acid in 26% and 13% yield, respectively.^{11,12)} The facts that *trans*-stilbene and benzoic acid were obtained from **1b** are important in elucidating the mechanisms for the arylation of alkenes¹⁰⁾ and carbonylation¹¹⁾ as well as carboxylation of arenes¹²⁾ by palladium(II) acetate.

Reaction of Palladium(II) Acetate with Dialkyl Sulfide in Toluene or in Thiophene. Treatment of palladium(II) acetate with diisobutyl sulfide in toluene at 80 °C for 2 h gave only an intractable oil. However, GLC analysis of the reaction mixture revealed the presence of bitolyls composed of six isomers [2,2':(2,3'+2,4'):3,3':3,4':4,4'=6:6:22:45:21] in 25% yield based on palladium(II) acetate. The above reaction carried out in thiophene also afforded an intractable oil, but bithienyls consisting of three isomers [2,2':(2,3'+3,3')=9:1] were detected in 25% yield based on palladium(II) acetate by GLC analysis. On the other hand, no coupling product was detected in a toluene or thiophene solution heated only with palladium(II) acetate at 80 °C for 2 h. In consideration of these facts, it seemed likely that tolyl- and thienyl-palladium species were formed during the reactions as intermediates, and that diisobutyl sulfide enhanced the coupling reactions of aromatic compounds.

Reactions of Palladium(II) Acetate with Phenyl-Substituted Dialkyl Sulfides, $\text{Ph}(\text{CH}_2)_n\text{SBu}'(n=1,2)$ in Benzene. It is interesting to investigate whether palladium(II) acetate could activate the C-H bond of benzene intermolecularly even in the presence of phenyl-substituted dialkyl sulfides or activate the ortho C-H bond of the phenyl group in the sulfides intramolecularly. The reaction of benzyl *t*-butyl sulfide with palladium(II) acetate in benzene at 80 °C afforded a cyclopalladated complex $[\{\text{Pd}(\mu\text{-MeCO}_2)(\text{C}_6\text{H}_4\text{CH}_2\text{SBu}'\text{-C}^1\text{S})\}_2]$ (**6**), whose IR and ^1H NMR spectra were identical with those of the authentic sample.¹⁹⁾ In contrast, *t*-butyl phenethyl sulfide afforded only an adduct, $[\text{Pd}(\text{MeCO}_2)_2(\text{Bu}'\text{SCH}_2\text{CH}_2\text{Ph})_2]$ (**7**) under the same reaction conditions. Prolonged heating of **7** in benzene at 50 °C for 20 h gave neither a cyclopalladated species nor a phenylpalladium one, but only **7** was recovered from the reaction mixture. Up to date, there has been only one report concerning the formation of six-membered cyclopalladated complexes of sulfur ligands.^{20,21)} In these cases, the sulfur-containing six-membered cyclopalladated structures were reinforced by the double chelations or a five-membered C-S or C-N chelate.²⁰⁾ It seemed likely that *t*-butyl phenethyl sulfide was also hard to be cyclopalladated and form a simple six-membered palladacycle $\text{Pd-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{-SBu}'\text{-C}^1\text{S}$.

Experimental

t-Butyl neopentyl sulfide,²²⁾ benzyl *t*-butyl sulfide,²³⁾ and *t*-butyl phenethyl sulfide²⁴⁾ were prepared according to the literatures. Diisobutyl, diisopropyl, diethyl, and di-*t*-butyl sulfides and tetrahydrothiophene were commercial samples. Gas chromatographic analyses were made with a Shimadzu GC-4B gas chromatograph using helium as a carrier gas on columns of Apieson Grease L and Silicone OV-17. Identification of the reaction products was performed by coinjection with authentic samples on the columns and by a Nichiden-Varian TE-600 gas chromatograph-mass spectrometer. For determination of yields, the following internal standards were used: naphthalene for biphenyls, bitolyls, and bithienyls, and hexamethylbenzene for benzoic acid. Other procedures were as described previously.²⁵⁾

Preparations of $[(\text{R}^1\text{SR}^2)\text{PhPd}(\mu\text{-MeCO}_2)_2\text{Pd}(\mu\text{-MeCO}_2)_2\text{-PdPh}(\text{R}^1\text{SR}^2)]$ (1a**; $\text{R}^1=\text{Bu}'$, $\text{R}^2=\text{CH}_2\text{Bu}'$; **1b**; $\text{R}^1=\text{R}^2=\text{Bu}'$; **1c**; $\text{R}^1=\text{R}^2=\text{Pr}^i$; **1d**; $\text{R}^1=\text{R}^2=\text{Et}$).** A mixture containing palladium(II) acetate (250 mg, 1.11 mmol) and *t*-butyl neopentyl sulfide (119 mg, 0.742 mmol) in 10 cm³ of benzene was heated at 70 °C for 90 min. After filtration, the filtrate was concentrated under reduced pressure and diluted with hexane to give 79 mg of **1a** as beige crystals. Complexes **1b**, **1c**, and **1d** were prepared similarly.

Reaction of **1a with Lithium Chloride.** Lithium chloride (103 mg, 2.43 mmol) in water (2 cm³) was added to an acetone solution (15 cm³) of **1a** (250 mg, 0.243 mmol), and the resulting mixture was stirred at room temperature for 6 h. After the mixture was evaporated to dryness, the residue was extracted with benzene. The extract was diluted with hexane to give 50 mg of $[\text{PdCl}_2(\text{Bu}'\text{SCH}_2\text{Bu}')_2]$ (**2**) as a yellow powder.

Reaction of **1a with Triethylphosphine and Lithium Bromide-Water (1/1).** Triethylphosphine (124 mg, 1.05 mmol) in acetone (5 cm³) was added to **1a** (150 mg, 0.146 mmol) in acetone (15 cm³), and the mixture was stirred at room temperature for 4 h. To the resulting yellow solution, lithium bromide-water (1/1) (507 mg, 5.84 mmol) was added. Stirring was further continued for 20 h, and then the mixture was evaporated to dryness. The residue was chromatographed on a silica-gel column (200 mesh, 1.8×16 cm). A yellow fraction eluted by benzene was collected and evaporated to dryness to give 44 mg of *trans*- $[\text{PdB}_2(\text{PET}_3)_2]$ (**3**). Another yellow fraction eluted by $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (3/1) afforded 28 mg of *trans*- $[\text{PdB}(\text{Ph})(\text{PET}_3)_2]$ (**4**).

Reactions of Palladium(II) Acetate with Di-*t*-butyl Sulfide or Tetrahydrothiophene in Benzene. A mixture containing palladium(II) acetate (250 mg, 1.11 mmol) and di-*t*-butyl sulfide (108 mg, 0.738 mmol) or tetrahydrothiophene (65 mg, 0.738 mmol) in benzene (15 cm³) was heated at 70 °C for 2 h. After the reaction mixture was filtered, the filtrate was concentrated under reduced pressure and diluted with hexane to give only dark brown oil in both cases.

Preparation of the Adduct $[\text{Pd}(\text{MeCO}_2)_2(\text{SR}^1\text{R}^2)_2]$ (5a**; $\text{R}^1=\text{Bu}'$, $\text{R}^2=\text{CH}_2\text{Bu}'$; **5c**; $\text{R}^1=\text{R}^2=\text{Pr}^i$).** A benzene solution (5 cm³) of *t*-butyl neopentyl sulfide (857 mg, 5.34 mmol) was added to a benzene solution (10 cm³) of palladium(II) acetate (400 mg, 1.78 mmol) at 5–10 °C. After stirring for 4 h at 10 °C, the resulting yellow solution was concentrated under reduced pressure and diluted with hexane to yield 180 mg of **5a**. Similarly, **5c** was prepared.

Reactions of **5a or **5c** with Benzene.** A benzene solution (10 cm³) of **5a** (150 mg, 0.275 mmol) was heated at 70 °C for 2 h and then filtered. The filtrate was concentrated under reduced pressure and diluted with hexane to afford 43 mg of **1a**. Complex **5c** was similarly converted to **1c**.

Reactions of **1b with Styrene, Carbon Monoxide, or Carbon Dioxide.** (i) **With Styrene.** Styrene (44 mg, 0.42 mmol) was added to a THF solution (10 cm³) of **1b** (200 mg, 0.200 mmol), and the resulting mixture was stirred at room temperature for 1 h. The mixture was filtered to remove the precipitated palladium black, and the filtrate was chromatographed on a silica-gel column (200 mesh, 1.8×30 cm). A fraction eluted by benzene/hexane (1/1) was collected and evaporated to dryness to give 68 mg of *trans*-stilbene as white crystals, whose IR, mp, and ^1H NMR spectrum were identical with those of the authentic sample.

(ii) **With Carbon Monoxide.** Carbon monoxide was bubbled through a THF solution (30 cm³) of **1b** (100 mg, 0.100 mmol) for 3 h at room temperature. Precipitated palladium black was filtered, and the filtrate was added to a saturated sodium hydrogencarbonate solution (10 cm³). Then, diethyl ether (15 cm³) was added. The water layer was separated and acidified with concentrated HCl and the organic product was extracted with diethyl ether (15 cm³). The ethereal layer was dried by Na_2SO_4 and after evaporation of the solvent, the product was analyzed and identified as benzoic acid by GLC analysis (64% based on **1b**), mp, and IR.

(iii) **With Carbon Dioxide.** In a 200-cm³ autoclave was placed a 100-cm³ beaker containing **1b** (213 mg, 0.213 mmol), THF (20 cm³), and acetic acid (5 cm³). The autoclave was closed, flushed with carbon dioxide, and pressurized to 4.4×10^6 Pa. The mixture was heated at 60 °C with stirring for 20 h. The resulting mixture was filtered and the filtrate

was similarly treated as described in (ii). The organic products detected by GLC analysis were benzoic acid (9% yield) and biphenyl (1% yield).

Reactions of Palladium(II) Acetate with Diisobutyl Sulfide in Toluene or Thiophene. A mixture containing palladium(II) acetate (150 mg, 0.668 mmol) and diisobutyl sulfide (65 mg, 0.445 mmol) in 10 cm³ of toluene or thiophene was heated at 70 °C for 2 h, and then filtered. The filtrate was concentrated under reduced pressure and diluted with hexane to give dark brown oil in both cases.

Reactions of Palladium(II) Acetate with Phenyl-Substituted Dialkyl Sulfides Ph(CH₂)_nSBu^t (n=1,2) in Benzene. (i) **With PhCH₂SBu^t.** A mixture containing palladium(II) acetate (150 mg, 0.670 mmol) and benzyl *t*-butyl sulfide (145 mg, 0.804 mmol) in benzene (10 cm³) was heated at 80 °C for 4 h, and then filtered. The filtrate was diluted with hexane to afford 50 mg of [{Pd(μ-MeCO₂)(C₆H₄CH₂SBu^t-C¹, S)}₂] (**6**) as a yellow powder.

(ii) **With PhCH₂CH₂SBu^t.** A mixture containing palladium(II) acetate (200 mg, 0.890 mmol) and *t*-butyl phenethyl sulfide (380 mg, 1.96 mmol) in benzene (20 cm³) was heated at 80 °C for 4 h, and then filtered. The filtrate was diluted with hexane to give 110 mg of [Pd(MeCO₂)₂-(Bu^tSCH₂CH₂Ph)₂] (**7**) as yellow crystals.

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