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Reactions of Chloro[4-[2-(methylthio)anilino]-3-penten-2-onato-*O*,*N*,*S*]palladium(II) with Carbanions and Pyridine Derivatives

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A Schiff base, 4-[2-(methylthio)anilino]-3-penten-2-one (Hmtap), prepared from acetylacetone and 2-(methylthio)aniline, reacted with $Na_2[PdCl_4]$ in the presence of sodium ethoxide to give [PdCl(mtap-*O*,*N*,*S*)] (**1**). Complex **1** was treated with carbanions formed from dimethyl malonate, methyl cyanoacetate, and malononitrile in the presence of sodium methoxide to afford the corresponding (disubstituted methyl)palladium(II) complexes, [Pd(CHYY′)(mtap-*O*,*N*,*S*)] (Y,Y′=COOMe and/or CN). On the other hand, **1** reacted with Tl(acac) to yield an *O*,*O*′-chelating complex, [Pd(mtap-*N*,*O*)(acac)], in which the mtap moiety served as a bidentate ligand. Moreover, **1** reacted with 2,2′-bipyridine (bpy) and 4-(dimethylamino)pyridine (dmapy) in the presence of $NaClO_4 \cdot H_2O$ to give [Pd(mtap-*N*,*O*)(bpy)]ClO_4 and [Pd(mtap-*O*,*N*,*S*)(dmapy)]ClO_4, respectively. These complexes are characterized by means of elemental analysis and IR and NMR spectroscopy.

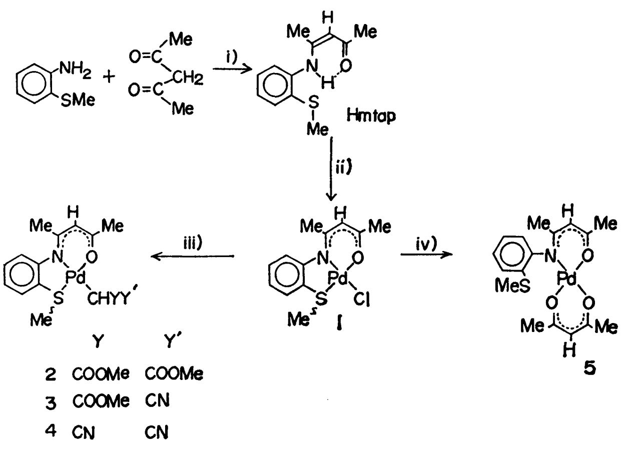
The previous papers from our laboratory revealed that Schiff bases, 4-(α-picolylamino)- and 4-[2-(diphenylphosphino)ethylamino]-3-penten-2-ones (Hpap and Hdpeap, respectively) reacted with $Na_2[PdCl_4]$ in the presence of base to yield [PdCl(pap-*N*,*N*,*O*)]¹⁾ and [PdCl(dpeap-*O*,*N*,*P*)],²⁾ respectively. In these square planar palladium(II) complexes, the Schiff bases served as a monoanionic tridentate ligand. Carbanions formed from active methylene compounds displaced the remaining chloro ligand at the fourth coordination site in the complexes to give (disubstituted methyl) palladium(II) complexes retaining the NNO- or ONP-typed tridentate chelate.¹,²⁾

It is interesting to investigate both the coordinating ability of sulfur atom in an ONS-typed chelate and the stabilizing effect of the chelate for the carbon-palladium σ-bond. In this paper, we present some palladium(II) complexes derived from reactions of chloro[4-[2-(methylthio)anilino]-3-penten-2-onato-*O*,*N*,*S*]palladium(II) [PdCl(mtap-*O*,*N*,*S*)] [mtap=4-[2-(methylthio)anilino]-3-penten-2-onato] with the carbanions or a few pyridine derivatives. Furthermore, the coordination ability of the sulfur atom in the mtap chelate and the stabilizing effect of the chelate for the C–Pd σ-bond were compared with the respective ones of the pap and dpeap chelates.

Results and Discussion

*Preparation of Hmtap and [PdCl(mtap-*O,N,S*)].* A mixture of 2-(methylthio)aniline and an excess amount of acetylacetone was refluxed to give colorless crystals of Hmtap in 84% yield. The spectroscopic data of Hmtap were quite consistent with its structure. Furthermore, it was possibly associated with the hydrogen-bonded keto-enamine form, by analogy with the cases of Hpap¹⁾ and other related Schiff bases.³⁾

After treating an ethanol solution of $Na_2[PdCl_4]$ with Hmtap in the presence of an equimolar amount of sodium ethoxide, the resulting red microcrystals were collected and assignable to [PdCl(mtap-*O*,*N*,*S*)] (**1**) (*vide infra*). In the ^1H-NMR spectrum of **1** in $CDCl_3$, methyl group on sulfur showed a downfield shift by 0.42 ppm due to the coordination to palladium.



Scheme 1. i) Reflux, ii) $Na_2[PdCl_4]+NaOC_2H_5$, iii) $CH_2YY'+NaOCH_3$, iv) Tl(acac).

Mass spectrum of **1** exhibited a parent-ion pattern centered at *m*/*e* 362, corresponding to [$^{106}Pd^{35}Cl$(mtap-*O*,*N*,*S*)]. In the far-infrared spectrum, there were two bands at 325 and 338 cm^{-1} for ν(Pd–^{37}Cl) and ν(Pd–^{35}Cl), respectively.

*Reactions of **1** with Carbanions Derived from Active Methylene Compounds.* Reactions of **1** with carbanions, formed from dimethyl malonate, methyl cyanoacetate, and malononitrile, were carried out in THF at room temperature to yield complexes, [Pd{$CH(CO_2CH_3)_2$}(mtap-*O*,*N*,*S*)] (**2**), [Pd{$CHCN(CO_2CH_3)$}(mtap-*O*,*N*,*S*)] (**3**), and [Pd{$CH(CN)_2$}(mtap-*O*,*N*,*S*)] (**4**), respectively, as shown in Scheme 1. No reaction occurred between **1** and a carbanion formed from ethyl nitroacetate, in analogy with the case of [PdCl(pap)] system.¹⁾ The complexes obtained in this study are considerably stable in the solid state in air. Yields, microanalytical data, and spectroscopic properties are summarized in Tables 1—3.

The IR spectra of **1**—**4**, as well as **5**—**8**,⁴⁾ showed three bands near 1560, 1515, and 1380 cm^{-1}, characteristic of 4-amino-3-penten-2-onato-*N*,*O* moiety. The ^1H-NMR spectra of **1**—**8** exhibited three singlets in the range of δ 1.35—2.9, ascribable to 1-, 5-, and sulfur-bonded methyl groups of the mtap moiety (Table

TABLE 1. YIELDS AND PROPERTIES OF THE PALLADIUM(II) COMPLEXES

Compound		Yield[a] / %	Mp[c] θ_m/°C	Found (Calcd) (%) H	C	N	Λ_M[d]
[PdCl(mtap-*O,N,S*)]	**1**	75[b]	160—163	3.87(3.90)	39.50(39.80)	3.87(3.87)	—
[Pd{CH(CO$_2$Me)$_2$}(mtap-*O,N,S*)]	**2**	48	191—192	4.60(4.62)	44.09(44.60)	3.00(3.06)	—
[Pd{CHCN(CO$_2$Me)}(mtap-*O,N,S*)]	**3**	68	179	4.35(4.27)	45.01(45.24)	6.48(6.59)	—
[Pd{CH(CN)$_2$}(mtap-*O,N,S*)]	**4**	37	175—178	3.85(3.86)	45.47(45.99)	10.83(10.73)	—
[Pd(mtap-*N,O*)(acac)]	**5**	17	155—157	5.07(4.97)	47.68(47.95)	3.04(3.29)	—
[Pd(mtap-*N,O*)(bpy)]ClO$_4$	**6**	70	196—198	3.84(3.81)	45.03(45.37)	7.08(7.22)	126
PdCl(mtap)(dmapy)	**7**	82	148	5.04(4.99)	46.90(47.12)	8.63(8.68)	59.5
[Pd(mtap-*O,N,S*)(dmapy)]ClO$_4$	**8**	77	102—115	4.65(4.41)	41.68(41.62)	7.78(7.66)	108

a) Based on **1**, unless noted elsewhere. b) Based on Na$_2$[PdCl$_4$]. c) With decomposition. d) Molar conductivity, Ω^{-1} cm^2 mol^{-1}, at 10^{-3} mol/l in acetonitrile solution at 25 °C.

TABLE 2. ^{1}H-NMR SPECTRA AND SELECTED IR BANDS

Complex	^{1}H-NMR Data[a] mtap[b] 1-CH$_3$	5-CH$_3$	*S*-CH$_3$	CH	Others[c]	IR Data $\tilde{\nu}$/cm^{-1} [i]
1	2.32	2.12	2.80	5.28	—	—
2	2.24	2.08	2.75	5.16	3.65(Me), 3.69(CH)	1718 ν(C=O), 1122 ν(C–O)
3[d]	2.28	2.08	2.81[e]	5.19	3.30(CH)[e], 3.68(Me)	2207 ν(C≡N), 1698 ν(C=O)
4	2.32	2.09	2.84	5.22	2.84(CH)	2222 s, 2170 w ν(C≡N)
5	2.00[f]	1.35	2.43	5.09[f]	1.73(Me), 2.09(Me)[f], 5.17(CH)[f]	1560 ν($\mathrm{C}\overset{\cdots}{-}\mathrm{O}$)
6	2.24	1.85	2.30	5.33	8.30d(bpy-H^6, H$^{6'}$)[g,h]	1608 ν(C=N)[j], 1093 (ClO$_4$)
7a	2.34	2.14	2.81	5.25	3.02(NMe$_2$), 6.43d(H$^\beta$)[g], 7.68d(H$^\alpha$)[g]	1618, 1573 ν(C=N)[j]
7b	2.06	1.69	2.40	5.22	2.87(NMe$_2$), 6.16d(H$^\beta$)[g], 7.60d(H$^\alpha$)[g]	1078, 1023 ν(C–N)
8	2.37	2.13	2.72	5.38	3.10(NMe$_2$), 6.66d(H$^\beta$)[g], 7.98d(H$^\alpha$)[g]	1617 ν(C=N)[j], 1091[k] ν(ClO$_4$)

a) δ Value (ppm) from TMS, in CDCl$_3$. Most of the signals, expect for ones noted elsewhere, appear as a singlet. b) Phenylene protons are omitted. c) Assignment is given in parentheses. d) Measured at 27 °C. See the text about the signals at −5 °C. e) A broad signal. f) Assigned tentatively because of similarity of the chemical shifts. g) Doublet [^3J(HH) = 7—8 Hz]. h) The other proton signals were observed at δ = 7.1—8.3 as multiplets. i) In CHCl$_3$ solution, except for **8**. See the text about the IR bands of the mtap moiety. j) Due to pyridine ring. k) In KBr disk.

TABLE 3. ^{1}H-DECOUPLED ^{13}C-NMR DATA OF THE PALLADIUM COMPLEXES[a]

Complex	mtap[b] 1-$\underline{\mathrm{C}}$H$_3$	5-$\underline{\mathrm{C}}$H$_3$	S$\underline{\mathrm{C}}$H$_3$	$\underline{\mathrm{C}}$H	$\underline{\mathrm{C}}\overset{\cdots}{-}\mathrm{N}$	$\underline{\mathrm{C}}\overset{\cdots}{-}\mathrm{O}$	Pd-CHYY′ $\underline{\mathrm{C}}$H	$\underline{\mathrm{C}}$=O	O$\underline{\mathrm{C}}$H$_3$	$\underline{\mathrm{C}}$≡N
2	25.9	24.3	27.5	104.4	163.4	180.9	32.3	174.2	50.9	—
3	25.7	24.4	27.8	104.6	163.7	180.7	12.2	174.3	51.9	122.4
4[c]	25.7	24.7	28.0	104.9	164.8	180.7	−10.6	—	—	119.8

a) δ value (ppm) from TMS. In CDCl$_3$, except for **4**. b) Phenylene carbon resonances are omitted. c) In CD$_2$Cl$_2$.

2). Among them, two resonances at the highest and an intermediate fields were assigned to 5- and 1-methyl protons of the 3-penten-2-onato-*N,O* moiety, respectively, on the basis of both analogy with the data for [Pd(CHYY′)(pap)] (Y,Y′ = CO$_2$CH$_3$ and/or CN)[1] and the difference of electronegativities of the nearly-located coordinating atoms, nitrogen and oxygen. This assignment was also supported by the {^{1}H}-^{13}C-NMR data of $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ groups (Table 3). The remaining resonance at the lowest field was unambiguously associated with the sulfur-bonded methyl group.

The ^{1}H-NMR spectra of **2**—**4** exhibited a singlet in the range of δ 2.8—3.7, assignable to a palladium-bonded methine proton (Table 2). As for **2**, there was a singlet at δ 3.65 for two esteric methyl groups with a satisfactory intensity implying their spectroscopic equivalence. In addition, its IR spectrum in chloroform showed only one ν(C=O) band at 1718 cm^{-1}, and the wave number was indicative of retention of esteric carbonyl groups without bonding of oxygen to hydrogen or palladium in an enol fashion. The IR spectrum of **4** exhibited a strong ν_{as}(C≡N) band at 2222 cm^{-1} together with a very weak ν_s(C≡N) one at 2170 cm^{-1}, attributable to a *C*-bonded dicyanomethyl group, Pd–CH(CN)$_2$ rather than an *N*-bonded 2-cyanoetheniminato one, Pd–N=C=CH–CN.[5] On the

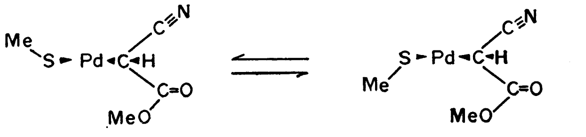
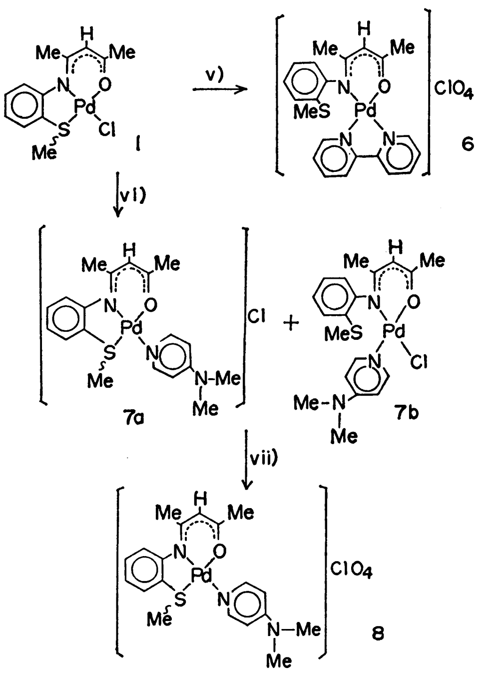


Fig. 1. Two configurational isomers of **3**. The 4-anilino-3-penten-2-onato-*O,N* moiety is deleted for simplification.

basis of these facts, **2**—**4** were concluded to have the structure with the carbon-palladium σ-bond, as shown in Scheme 1. The ^{1}H-decoupled ^{13}C-NMR data are fully consistent with the *C*-bonded structure (Table 3). The methine carbons bonded to palladium appeared as a singlet at δ 32.3 for **2**, at δ 12.2 for **3**, and at δ −10.6 for **4**. It is noteworthy that the higher-field resonances of the methine carbons in **3** and **4** are reasonably correlated to the smaller deshielding effect of the cyano group as compared with that of ester group,[6] together with the shielding effect by palladium through the σ-bond. A similar high-field shift was observed in the case of [Pd{CH(CO_2R)Z}(pap)] (Z=$CO_2C_2H_5$ or CN).[1] As for three methyl carbon resonances in the range of δ 24—28, two singlets near δ 24.5 and 25.8 were attributable to 5- and 1-methyl carbons of the 3-penten-2-onato-*N,O* moiety on the analogy of their chemical shifts to the coorresponding data of [Pd{CH(CO_2R)Z}(pap)].[1] Especially, the singlet near δ 25.8 was associated with the 1-methyl carbon on the basis of both the actual coincidence of the chemical shift with the corresponding value for [Pd{CH(CO_2R)Z}(pap)][1] and the difference of the electronegativities of the nearly-located coordinating atoms (*vide ante*). The third singlet near δ 27.8 was ascribed to sulfur-bonded methyl carbon.

The configuration of **3** is diastereotopic leading to two configurational isomers, because of the sp^3 sulfur atom and the asymmetric carbon bonded to palladium. It is notable that **3** showed temperature-dependent ^{1}H-NMR spectra. At 27 °C, **3** showed two slightly broad signals at δ 2.81 (3H, $S\underline{CH_3}$) and 3.30 (1H, Pd–$\underline{CH}$) and a sharp singlet at δ 2.08 (3H, 5-$\underline{CH_3}$), as seen in Table 2. Each of these three signals separated into two considerably sharp singlets at −5 °C; $S\underline{CH_3}$ at δ 2.85 (2.4 H) and 2.68 (0.6H); Pd–$C\underline{H}$ at δ 3.32 (0.8H) and 3.22 (0.2H); and 5-$C\underline{H_3}$ at δ 2.09 (2.4H) and 2.07 (0.6H).[7] These data indicate that inversion of the sulfur-bonded methyl group in **3** took place rapidly on the NMR time scale above room temperature and that the two configurational isomers, as shown in Fig. 1, were fixed in the population ratio of about 4:1 at −5 °C, owing to the quenching of the inversion. Similar configurational change at sulfur atom has been observed as regards (dialkyl sulfide)-palladium(II) complexes.[8–10]

In sharp contrast to the cases of carbanions derived from dimethyl malonate, methyl cyanoacetate and malononitrile, **1** reacted with Tl(acac) to give an *O,O'*-chelated acetylacetonato complex, **5**. This structure was confirmed by the lack of ν(C=O) band of free carbonyl groups and by a singlet resonance at δ 5.09 characteristic of the methine proton of the *O,O'*-chelated acetylacetonato moiety. Dissociation of sulfur



Scheme 2. v) 2,2'-Bipyridine+$NaClO_4$, vi) dmapy, vii) $NaClO_4\cdot H_2O$.

donor in the mtap moiety from palladium by the incoming acac chelate was shown by the upfield shift of the *S*-methyl proton resonance by *ca.* 0.4 ppm. In addition, 5-methyl protons of **5** resonated at a higher field by *ca.* 0.6 ppm than those of **1**—**4**. This upfield shift was attributed to the anisotropic effect due to the phenylene ring, lying actually perpendicular to the coordination plane. The dpeap complex, [PdCl(dpeap-*O,N,P*)] reacted easily with Tl(acac) in CH_2Cl_2 at room temperature to yield a (diacetylmethyl)palladium(II) complex involving a palladium-carbon σ-bond stabilized by the phosphine.[2] It has been reported that triphenylphosphine and pyridine also stabilized the diacetylmethyl-palladium(II) bond.[11,12] On the other hand, our present mtap system could not furnish a stabilizing field enough to produce the (diacetylmethyl)palladium(II) complex, and labile coordination property of the sulfur donor helped the formation of the *O,O'*-chelated structure. In our previous research,[1] Tl(acac) did not react with [PdCl(pap)] under THF reflux, owing to rigid coordinate bonds to palladium.

Reactions of 1 with Pyridine Derivatives. Dissociation of the *S*-donor from palladium in **5** led us to undergo the reactions of **1** with some pyridine derivatives in order to elucidate the coordination behavior of the *S*-donor to palladium. When **1** was treated with excess 4-picoline in THF at room temperature, no 4-picoline adduct to **1** was isolated. On the other hand, the ^{1}H-NMR spectrum of a mixture of **1** and 2,2'-bipyridine (bpy) (1:1) exhibited signals corresponding to two species of [PdCl(mtap-*O,N,S*)] and [Pd(mtap-*N,O*)(bpy)]Cl in a ratio of 73:27, indicating the following equilibrium.

$$[\mathrm{PdCl(mtap}\text{-}\mathit{ON,S})] + \mathrm{bpy} \rightleftharpoons [\mathrm{Pd(mtap}\text{-}\mathit{N,O})(\mathrm{bpy})]\mathrm{Cl}$$

Preference of 2,2'-bipyridine to bidentate coordination brought about the equilibrium leading to [Pd(mtap-

N,O)(bpy)]Cl with the dissociation of the *S*-donor. The dissociation of the *S*-donor in [Pd(mtap-*N,O*)(bpy)]Cl was determined easily by the chemical shift of the *S*-methyl proton resonance. The mixture of the two species was converted quantitatively to [Pd(mtap-*N,O*)(bpy)]ClO_4 (**6**) by treatment with $NaClO_4 \cdot H_2O$ in THF at room temperature (Scheme 2).

Complex **1** was also treated with a slight excess of 4-(dimethylamino)pyridine (dmapy), a well-known strong base, in THF at room temperature to give a pale yellow powder (**7**), which was suggested as a 1:1 adduct of **1** with dmapy by its elemental analysis. Moreover, the ^{1}H-NMR spectrum of **7** in $CDCl_3$ revealed the coexistence of two isomers, which are [Pd(mtap-*O,N,S*)(dmapy)]Cl (**7a**) and [PdCl(mtap-*N,O*)(dmapy)] (**7b**) in a ratio of 55:45. *S*-Methyl proton resonances unambiguously indicated the retention of the *S*-donor coordination to palladium in **7a** and dissociation of the *S*-donor in **7b**. An ionic complex, [Pd(mtap-*O,N,S*)(dmapy)]ClO_4 (**8**), was obtained quantitatively from the mixture of **7a** and **7b** and $NaClO_4 \cdot H_2O$. Transformation of **7b** to **8** proceeded reasonably through **7a**. These results indicate that the *S*-donor in **1** is relatively labile and can be displaced by the strong nucleophile or the multidentate ligand. In the case of 4-picoline, nucleophilicity is not enough, together with its non-chelate structure.

Experimental

Materials and General Proceduces. 2-(Methylthio)aniline[13)] and thallium(I) acetylacetonate[14)] were prepared by the respective literature methods. Solvents were dried by the standard methods and distilled. Preparative operations were performed under nitrogen. ^{13}C-NMR spectra were recorded on JEOL FX-90-Q, using tetramethylsilane as an internal standard. Mass spectra were obtained with a Nichiden-Varian TE-600 gas chromatograph-mass spectrometer. IR and ^{1}H-NMR spectra, melting points, and molar conductivities were measured according to the methods described in the previous paper.[1)] The temperature of the NMR samples was determined with methanol or 1,3-propanediol.

Preparation of 4-[2-(Methylthio)anilino]-3-penten-2-one (Hmtap). A mixture of 2-(methylthio)aniline (0.13 mol) and acetylacetone (0.33 mol) was refluxed for 3 h with removal of liberated water. Unreacted starting materials were removed under *ca.* 0.5 mmHg (1 mmHg≈133.322 Pa) at *ca.* 100 °C, and the residue was recrystallized from dichloromethane and hexane to yield colorless crystals of Hmtap: Found: C, 65.18; H, 6.96; N, 6.33%; M$^+$, 221. Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.33%; M, 221.32. Mp 58 °C: IR ($CHCl_3$) 3375 (NH), 1616, 1566, and 1518 cm^{-1} (α,β-unsaturated β-amino ketone); ^{1}H-NMR ($CDCl_3$) δ= 1.85 (3H, s, CH_3), 2.10 (3H, s, CH_3), 2.38 (3H, s, SCH_3), 5.22 (1H, s, CH), 7.0—7.4 (4H, m, aromatic CH), and 12.20 (1H, broad, NH).

*Preparation of [PdCl(mtap-*O,N,S*)] 1.* An ethanol solution of sodium ethoxide (6.1 mmol) was added slowly to a mixture of $Na_2[PdCl_4]$ (6.1 mmol) and Hmtap (6.8 mmol) in ethanol (150 ml). After stirring at room temperature for 16 h, the solvent was removed under vacuum. Recrystallization of the residue from dichloromethane and hexane gave red microcrystals of ***1***.

Reactions of 1 with Carbanions Formed from Active Methylene Compounds. Dimethyl malonate (0.80 mmol) in THF was treated with sodium methoxide (0.96 mmol), followed by slow addition of **1** (0.80 mmol) in THF. The mixture was stirred for 27 h at room temperature, and the solvent was removed under vacuum. The residue was recrystallized from dichloromethane and hexane to yield brown microcrystals of [Pd{CH($COOCH_3$)$_2$}(mtap-*O,N,S*)] (**2**). Complex **1** reacted similarly with methyl cyanoacetate and malononitrile to afford reddish orange microcrystals of [Pd{CHCN(CO_2CH_3)}(mtap-*O,N,S*)] (**3**) and orange ones of [Pd{CH(CN)$_2$}(mtap-*O,N,S*)] (**4**), respectively.

Reaction of 1 with Thallium Acetylacetonate. Thallium(I) acetylacetonate (1.0 mmol) was added in portions to a dichloromethane solution (10 ml) of **1** (0.8 mmol) and the mixture was stirred for 30 h under reflux. After the solvent was evaporated *in vacuo*, the residue was recrystallized from benzene and hexane, yielding light-brown microcrystals of [Pd(mtap-*N,O*)(acac)] (**5**).

Reaction of 1 with 2,2′-Bipyridine. Sodium perchlorate–water(1/1) (0.69 mmol) was added to a THF suspension of **1** (0.69 mmol) and 2,2′-bipyridine (0.89 mmol), and the mixture was stirred for 20 h at room temperature. The solvent was removed under vacuum, and the recrystallization of the residue from dichloromethane and hexane gave a pale yellow powder of [Pd(mtap-*N,O*)(bpy)]ClO_4 (**6**).

Reaction of 1 with 4-(Dimethylamino)pyridine. 4-(Dimethylamino)pyridine (1 mmol) was added to a THF (20 ml) suspension of **1** (0.83 mmol) and the color turned into orange-yellow. After stirring for 20 h at room temperature, a pale yellow precipitate was collected and washed with diethyl ether and hexane to give PdCl(mtap)(dmapy) (**7**). A THF (20 ml) suspension of **7** was treated with sodium perchlorate–water(1/1) in a molar ratio of 1:1.2, followed by stirring at room temperature for several hours. After filtration and removal of the solvent from the filtrate, the residue was recrystallized from dichloromethane and diethyl ether, and [Pd(mtap-*O,N,S*)(dmapy)]ClO_4 (**8**) was isolated as red microcrystals.

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