appearance of a black dispersion (may be palladium black), and most of the reaction was completed within 20 min. After the carbon monoxide was purged, the reaction mixture was filtered, and the solvent was removed at 0 °C under vacuum. The residue was extracted several times with hexane at 30–35 °C when a sodium aliphatic carboxylate was used. The products were obtained by crystallization of the cooled hexane extracts or by removal of hexane under vacuum. When sodium benzoate was used, the solid residue was washed successively with small amounts of acetonitrile, water, and petroleum ether at 0 °C and dried under vacuum. Rapid short-pass distillation below 50 °C (bath temperature) in vacuo (0.5 mmHg) gave almost pure products in the case of benzoic acetic and *p*-toluic acetic anhydride with about 80% recovery. Since the purity of the distillates of other liquid products was similar to that of the crude concentrates, the yields of entries 1 and 3–5 listed in Table I were those of the concentrates. ^{1}H NMR spectral data of mixed acid anhydrides are summarized in Table IV. The characteristic features in IR and ^{1}H NMR spectra caused by the contamination with homo acid anhydrides and acids are described in the text and the footnote of Table I. Anal. PhCOOCOMe, calcd for $C_9H_8O_3$: C, 68.85; H, 4.88. Found: C, 66.16; H, 4.88. 4-I-C_6H_4COOCOMe, calcd for $C_9H_7O_3I$: C, 37.27;, H, 2.43. Found: C, 37.14; H, 2.43. 3-NO_2-C_6H_4COOCOMe, calcd for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.66; H, 3.37; N, 7.00. 4-NO_2-C_6H_4COOCOMe, calcd: C, 51.68; H, 3.37; N, 6.70. Found: C, 51.33; H, 3.24; N, 6.96.

The structure of **3** (R = Ph) was also confirmed by comparison of IR spectra with those of authentic samples prepared by a published method.[7]

Arenecarboxylic Anhydrides (4). An arenecarboxylic acetic anhydride (1 g) was placed in a 30-mL round-bottomed flask and heated at 100–120 °C for 0.5–1 h under vacuum (ca. 10 mmHg), and the residue was distilled by means of a Kugelrohr distillation apparatus (ca. 3 mmHg). The structures of compounds **4** were confirmed by comparison of IR spectra with those of authentic samples prepared by the ordinary method from the corresponding arenecarboxylic acid.

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Aromatic Carboxamides. To a filtered mixture (see the general procedure) was added an amine (3 mL) at 0 °C, and the mixture was stirred for 2 h at room temperature. After removal of the solvent, 100 mL of ether was added, and the mixture was washed with aqueous sodium carbonate, 1 N hydrochloric acid, and aqueous sodium chloride, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was recrystallized (for anilides) or distilled (for *N,N*-diethyl amides).

Satisfactory IR and ^{1}H NMR spectra were obtained for all products produced by this method. For 4-EtOCO-C_6H_4CONHPh: ^{1}H NMR (Me_4Si, $CDCl_3$), 1.43 (t, 3 H), 4.38 (q, 2 H, J = 7 Hz), 7.1–7.7 (m, 5 H), 7.88 (d, 2 H), 8.08 ppm (d, 2 H, J = 9 Hz). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.03; H, 5.64; N, 5.15.

Registry No. **1** (Ar = Ph), 369-57-3; **1** (Ar = 3-MeC_6H_4), 1422-76-0; **1** (Ar = 4-MeC_6H_4), 459-44-9; **1** (Ar = 2-MeOC_6H_4), 492-95-5; **1** (Ar = 4-BrC_6H_4), 673-40-5; **1** (Ar = 4-IC_6H_4), 1514-50-7; **1** (Ar = 3-$NO_2C_6H_4$), 586-36-7; **1** (Ar = 4-$NO_2C_6H_4$), 456-27-9; **1** (Ar = 1-naphthyl), 28912-93-8; **2** (R = H), 141-53-7; **2** (R = Me), 127-09-3; **2** (R = Et), 137-40-6; **2** (R = Bu-*t*), 1184-88-9; **2** (R = Ph), 532-32-1; **3** (Ar = Ph; R = Me), 2819-08-1; **3** (Ar = 4-IC_6H_4; R = Me), 75474-02-1; **3** (Ar = 3-$NO_2C_6H_4$; R = Me), 4015-57-0; **3** (Ar = 4-$NO_2C_6H_4$; R = Me), 75474-03-2; **3** (Ar = Ph; R = H), 78823-32-2; **3** (Ar = Ph; R = Et), 50998-43-1; **3** (Ar = Ph; R = Bu-*t*), 19820-60-1; **3** (Ar = 3-MeC_6H_4; R = Me), 78823-33-3; **3** (Ar = 4-MeC_6H_4; R = H), 78823-34-4; **3** (Ar = 4-MeC_6H_4; R = Me), 75474-00-9; **3** (Ar = 2-MeOC_6H_4; R = Me), 78823-35-5; **3** (Ar = 4-BrC_6H_4; R = Me), 75474-01-0; **3** (Ar = 4-BrC_6H_4; R = Ph), 75474-04-3; **3** (Ar = 4-$NO_2C_6H_4$; R = Et), 78823-36-6; **3** (Ar = 4-$NO_2C_6H_4$; R = Ph), 75474-05-4; **3** (Ar = 1-naphthyl; R = Ph), 73368-15-7; **4** (Ar = Ph), 93-97-0; **4** (Ar = 3-MeC_6H_4), 21436-44-2; **4** (Ar = 4-MeC_6H_4), 13222-85-0; **4** (Ar = 2-MeOC_6H_4), 794-94-5; **4** (Ar = 4-BrC_6H_4), 1633-33-6; **4** (Ar = 4-IC_6H_4), 75474-06-5; **4** (Ar = 3-$NO_2C_6H_4$), 69859-37-6; **4** (Ar = 4-$NO_2C_6H_4$), 902-47-6; 4-EtOCOC_6H_4COOCO-*t*-Bu, 78823-37-7; 4-MeC_6H_4COOCO-*t*-Bu, 78823-38-8; 4-BrC_6H_4COOCO-*t*-Bu, 78823-39-9; 4-$NO_2C_6H_4$COOCO-*t*-Bu, 78823-40-2; 4-MeOC_6H_4COOCO-*t*-Bu, 78823-41-3; PhCONHPh, 93-98-1; 4-EtOCOC_6H_4CONHPh, 78823-42-4; PhCONEt_2, 1696-17-9; 4-BrC_6H_4CONEt_2, 5892-99-9; 4-MeC_6H_4CONEt_2, 2728-05-4; 4-$NO_2C_6H_4$CONEt_2, 5323-47-7; 4-MeOC_6H_4CONEt_2, 7465-86-3; Pd, 7440-05-3; $PhNH_2$, 62-53-3; Et_2NH, 109-89-7.

Ortho Vinylation of Aromatic Amides via Cyclopalladation Complexes[1]

Hiroshi Horino* and Naoto Inoue

Department of Chemistry, College of General Education, Tohoku University, Kawauchi, Sendai 980, Japan

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The reaction of acetanilide and meta- and para-substituted acetanilides with palladium acetate has given new ortho-palladated complexes **2a–j**, which reacted with carbon monoxide, ethylene, or methyl vinyl ketone to produce the corresponding *N*-acylanthranilic esters **4a–m**, 2-acetaminostyrenes **9k–p**, and 4-aryl-3-buten-2-one derivatives **9a–j**, respectively. Reactions of **2a** with substituted olefins proceeded readily to give the 2-[(acetylamino)phenyl] olefins **8a–h**. Ortho-substituted acetanilides and *N*-methylacetanilide did not undergo complex formation with palladium acetate.

Investigations of ortho-metalated complexes of various aromatic compounds[2] have opened new routes in organic synthesis. Reactions of carbon monoxide[3] or isocyanide[4] with metal complexes of α-aryl nitrogen derivatives have led to syntheses of heterocyclic compounds. Reaction of ortho-palladated complexes with organolithium or Grignard reagents results in regiospecific carbon–carbon bond formation.[5] Insertion reactions with olefins[6] or acetylenes[7]

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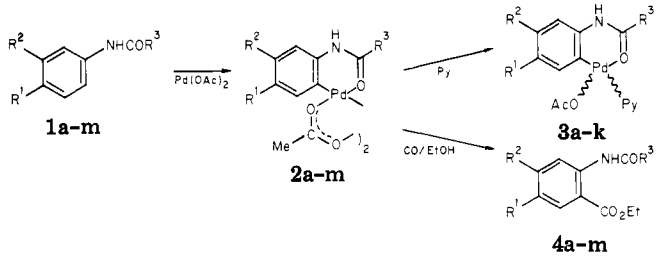
Table I. Palladium Complexes 2a-m and Products of Their Reaction with Pyridine and with Carbon Monoxide



R¹	R²	R³	amide	complex dimer 2 (yield, %)	pyridine complex 3 yield, %	pyridine complex 3 mp °C dec	ester 4 (yield, %)
H	H	Me	1a	2a (99)	3a (97)	181	4a (79)
Me	H	Me	1b	2b (59)	3b (100)	192[a]	4b (49)
OMe	H	Me	1c	2c (68)	3c (77)	183[b]	4c (65)
Cl	H	Me	1d	2d (83)	3d (66)	204[c]	4d (68)
CO_2Et	H	Me	1e	2e (74)	3e (74)	188[d]	4e (68)
COMe	H	Me	1f	2f (94)	3f (82)	192[e]	4f (74)
H	Me	Me	1g	2g (72)	3g (86)	190[f]	4g (61)
H	OMe	Me	1h	2h (38)	3h (27)	171[g]	4h (30)
H	Cl	Me	1i	2i (74)	3i (66)	220	4i (99)
H	CO_2Me	Me	1j	2j (63)	3j (92)	192[h]	4j (44)
H	H	Et	1k	2k (79)	3k (61)	180[i]	4k (88)
H	H	*i*-Pr	1l	2l (93)			4l (71)
H	H	*t*-Bu	1m	2m (43)			4m (52)
H	H	CH_2=CH	1n		no complex formation		
H	H	Ph	1o		no complex formation		

[a] Anal. Calcd for $C_{16}H_{18}O_3N_2Pd$: C, 48.89; H, 4.62; N, 7.13. Found: C, 48.05; H, 4.65; N, 6.88. [b] Anal. Calcd for $C_{16}H_{18}O_4N_2Pd$: C, 46.98; H, 4.43; N, 6.85. Found: C, 47.06; H, 4.65; N, 6.64. [c] Anal. Calcd for $C_{15}H_{15}O_3N_2ClPd$: C, 43.57; H, 3.66; N, 6.78. Found: C, 43.55; H, 3.88; N, 6.74. [d] Anal. Calcd for $C_{18}H_{20}O_5N_2Pd$: C, 47.93; H, 4.47; N, 6.21. Found: C, 47.52; H, 4.47; N, 5.94. [e] Anal. Calcd for $C_{17}H_{18}O_4N_2Pd$: C, 48.49; H, 4.31; N, 6.66. Found: C, 47.55; H, 4.33; N, 6.02. [f] Anal. Calcd for $C_{16}H_{18}O_3N_2Pd$: C, 48.89; H, 4.62; N, 7.13. Found: C, 48.38; H, 4.60; N, 6.96. [g] Anal. Calcd for $C_{16}H_{18}O_4N_2Pd$: C, 46.98; H, 4.43; N, 6.85. Found: C, 47.08; H, 4.44; N, 6.81. [h] Anal. Calcd for $C_{17}H_{18}O_5N_2Pd$: C, 46.72; H, 4.15; N, 6.41. Found: C, 46.31; H, 4.25; N, 6.28. [i] Anal. Calcd for $C_{16}H_{18}O_3N_2Pd$: C, 48.89; H, 4.62; N, 7.13. Found: C, 48.60; H, 4.59; N, 6.97.

have led to vinylic substitution of allyl and aromatic palladium complexes.

Selective ortho functionalization of aromatic amides has been reported.[8] Synthesis of substituted styrenes, including the *o*-methyl, *o*-nitro, and *o*-amino derivatives, has been achieved by reaction of the corresponding aromatic bromo compounds with ethylene and triethylamine under pressure in the presence of a catalyst comprised of $Pd(OAc)_2$ and tri-*o*-tolylphosphine.[9a] In addition, palladium- or rhodium-catalyzed reactions of aniline with ethylene under pressure have given quinaldine; an ortho-metalated complex of aniline was postulated as an intermediate in this reaction.[9b] This paper reports the preparation and characterization of ortho-palladated complexes of acetanilides and some ring-substituted acetanilides and their reactions with carbon monoxide and with olefins.

Results and Discussion

Reaction of acetanilide (**1a**) with a stoichiometric amount of $Pd(OAc)_2$ in refluxing toluene gave a greenish yellow complex, **2a**, which was shown to be di-μ-acetato-bis(2-acetaminophenyl-*2C,O*)dipalladium(II) (**2a**) by its IR and NMR spectra and its chemical behavior set forth in Scheme I and in Table I. Reduction of **2a** with $NaBH_4$ or hydrogen converted it to **1a** and palladium metal. Treatment of **2a** with bromine yielded *o*-bromoacetanilide exclusively. Since bromination of **1a** usually gives *p*-bromoacetanilide,[10] **2a** must be an ortho-palladated complex of **1a**. Addition of pyridine to **2a** afforded a monomeric complex **3a**. Carbonylation of **2a** in ethanol occurred under mild conditions to give ethyl *N*-acetylanthranilate (**4a**). When a mixture of **2a** and LiCl in aqueous acetone was stirred, the acetoxyl ligand of **2a** was replaced by chloride to form chloropalladium complex **5a**. A complex corresponding to **5a** was first reported from the reaction of **1a** and $PdCl_2$ in aqueous methanol by Cameron and Kilner,[11] who assigned it the structure **5a** on the basis of its IR spectrum. However, our attempts to prepare it under their conditions gave only bis(aniline)dichloropalladium.[12]

Reactions of meta- or para-substituted acetanilides with $Pd(OAc)_2$ gave the corresponding ortho-palladated complexes **2b–j** (Table I). The presence of either electron-donating or electron-withdrawing groups on the aromatic ring of the amide had no significant influence on the yields of **2b–j**. Higher temperatures or prolonged reactions led to formation of palladium black as did exposure of the reaction mixture to air. As some of **2b–j** were too unstable for purification, all of them were converted to the stable pyridine complexes **3b–j**, which were recrystallized and characterized by spectral data and elemental analyses. Ethanolic solutions of **2b–j** were treated with carbon monoxide to give the corresponding *N*-acetylanthranilic

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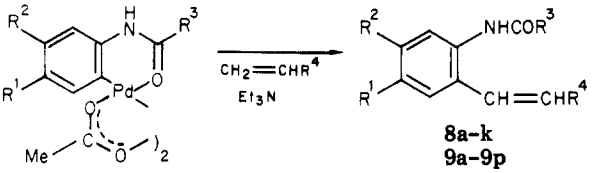
Table II. Reaction of 2a-m with Olefins and Physical Properties of the Products[a]



2a-g,i-k,m

8a-k
9a-9p

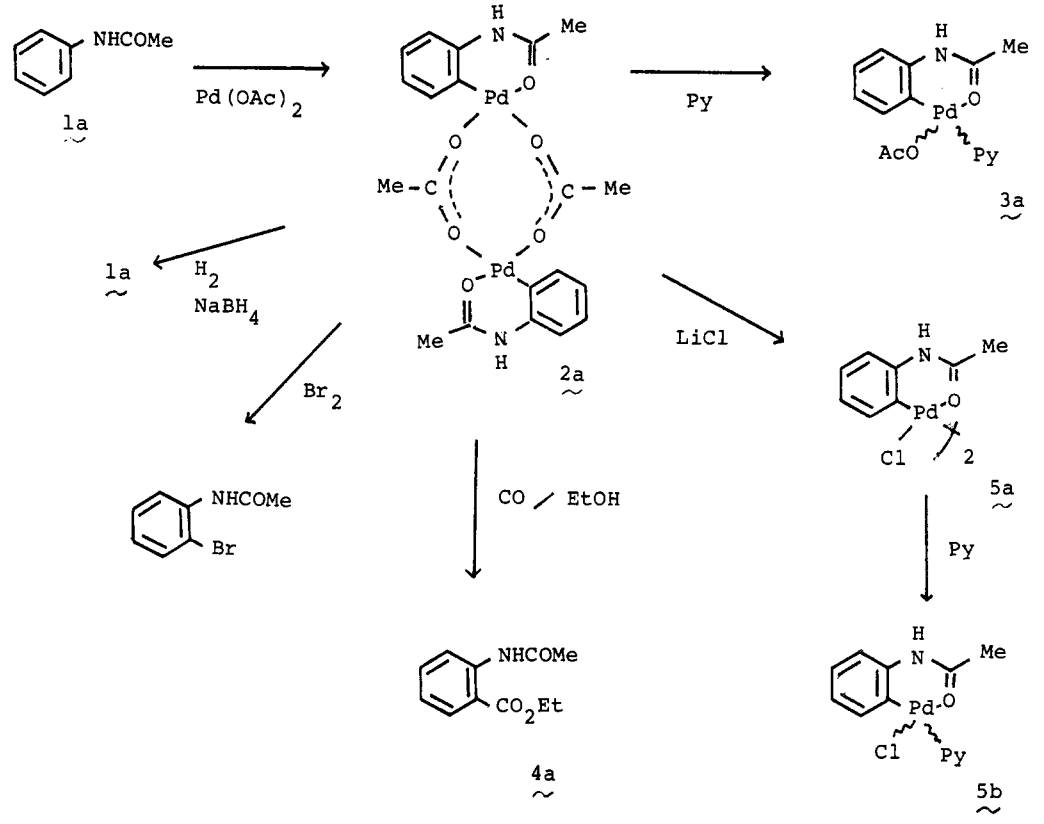
complex	R^1	R^2	R^3	R^4	product	yield, %	mp, °C	IR (KBr), cm^{-1}	NMR ($CDCl_3$) δ (J, Hz)
2a	H	H	Me	Ph	8a	52	141-142[b]	3220 (NH), 1645 (NAc)	2.12 (NAc, s), 6.9-7.8 (aromatic and vinylic)
2a	H	H	Me	3,4-$OCH_2OC_6H_3$	8b	43	185-186[c]	3300 (NH), 1650 (NAc)	2.18 (NAc, s), 5.90 (OCH_2O, s), 6.6-7.8 (aromatic and vinylic)
2a	H	H	Me	3-AcO-4-$MeOC_6H_3$	8c	80	135-137[d]	3230 (NH), 1770 (OAc), 1655 (NAc)	2.09 (NAc, s), 2.28 (OAc, s), 3.77 (OMe, s), 6.7-7.8 (aromatic and vinylic)
2a	H	H	Me	CN	8d	57	171-172[d,f]	3270 (NH), 2210 (CN), 1660 (NAc)	2.18 (NAc, s), 5.75 (d, J = 16), 7.1-7.8 (aromatic)
2a	H	H	Me	$CH(OEt)_2$	8e	40[g]	163-164[b]	3280 (NH), 1685 (CHO), 1655 (NAc)	2.18 (NAc, s), 7.2-7.8 (aromatic), 9.70 (CHO, d, J = 8)
2a	H	H	Me	CO_2Me	8f	49	136-137[d]	3280 (NH), 1720 (ester), 1660 (CO)	2.17 (NAc, s), 3.77 (OMe, s), 6.33 (d, J = 16), 7.1-7.9 (aromatic)
2a	H	H	Me	COMe	8g	83	126-127[e]	3250 (NH), 1685 (NAc), 1660 (CO)	2.13 (NAc, s), 2.29 (Me, s), 6.56 (d, J = 16), 7.1-7.8 (aromatic)
2a	H	H	Me	OAc	8h	44	158[e]	3270 (NH), 1770 (OAc), 1660 (NAc)	2.02 (OAc, s), 2.12 (NAc, s), 6.35 (d, J = 15), 7.0-7.7 (aromatic)
2b	Me	H	Me	COMe	9a	67	173[h]	3220 (NH), 1655 (NAc), 1650 (CO)	2.27 (NAc, s), 2.34 (Me, s), 2.58 (Me, s), 6.71 (d, J = 16), 7.5-8.1 (aromatic)
2c	OMe	H	Me	COMe	9b	62	186-187[i]	3230 (NH), 1660 (NAc), 1645 (CO)	2.27 (NAc, s), 2.40 (Me, s), 3.88 (OMe, s), 6.65 (d, J = 16), 6.9-7.8 (aromatic)
2d	Cl	H	Me	COMe	9c	94	170[c]	3330 (NH), 1660 (NAc), 1630 (CO)	2.21 (NAc, s), 2.34 (Me, s), 6.64 (d, J = 14), 7.2-7.8 (aromatic)
2e	CO_2Et	H	Me	COMe	9d	40	115[d]	3270 (NH), 1705 (ester), 1675 (NAc)	1.40 (Et, t), 2.23 (Me, s), 2.33 (Me, s), 4.37 (Et, q), 6.68 (d, J = 15), 7.5-8.2 (aromatic)
2f	COMe	H	Me	COMe	9e	63	181-183[h]	3260 (NH), 1680 (Ac), 1650 (NAc), 1635 (CO)	2.48 (NAc, s), 2.57 (Me, s), 2.70 (Me, s), 6.94 (d, J = 16), 7.87 (d, J = 16), 8.1-8.35 (aromatic)
2g	H	Me	Me	COMe	9f	980	151-152[h]	3280 (NH), 1680 (NAc), 1660 (CO)	2.27 (NAc, s), 2.29 (Me, s), 6.53 (d, J = 16), 6.9-7.7 (aromatic)
2i	H	Cl	Me	COMe	9g	77	158[e]	3370 (NH), 1680 (NAc), 1660 (CO)	2.21 (NAc, s), 2.33 (Me, s), 6.58 (d, J = 15), 7.0-7.8 (aromatic)
2j	H	CO_2Me	Me	COMe	9h	53	181[h]	3260 (NH), 1735 (ester), 1675 (CO)	2.20 (NAc, s), 2.33 (Me, s), 3.89 (OMe, s), 6.61 (d, J = 16), 7.4-8.0 (aromatic)
2k	H	H	Et	COMe	9i	86	117-118[d]	3280 (NH), 1675 (NAc), 1650 (CO)	1.22 (Et, t), 2.28 (NAc, s), 2.40 (Et, q), 6.56 (d, J = 16), 7.1-7.7 (aromatic)
2m	H	H	*t*-Bu	COMe	9j	71	118-119[j]	3300 (NH), 1670 (NAc), 1650 (CO)	1.33 (*t*-Bu, s), 2.31 (NAc, s), 6.60 (d, J = 16), 7.1-7.7 (aromatic)
2a	H	H	Me	H	9k	70	90.5-91.5[n]	3230 (NH), 1645 (NAc)	2.16 (NAc, s), 5.35 (d, J = 11), 5.56 (d, J = 17), 6.72 (dd, J = 11, 17), 7.1-7.9 (aromatic)

Table II (*Continued*)

complex	R^1	R^2	R^3	R^4	product	yield, %	mp, °C	IR (KBr), cm^{-1}	NMR ($CDCl_3$) δ (J, Hz)
2b	Me	H	Me	H	9l	62	98-99[l]	3280 (NH), 1660 (NAc)	2.12 (NAc, s), 3.20 (Me, s), 5.30 (d, J = 10), 5.58 (d, J = 17), 6.72 (dd, J = 10, 17), 6.9-7.7 (aromatic)
2c	OMe	H	Me	H	9m	54	105-106[l]	3230 (NH), 1640 (NAc)	2.13 (NAc, s), 3.77 (OMe, s), 5.30 (d, J = 11), 5.58 (d, J = 17), 6.73 (dd, J = 17, 11), 6.7-7.5 (aromatic)
2d	Cl	H	Me	H	9n	43	110[l]	3260 (NH), 1655 (NAc)	2.16 (NAc, s), 5.46 (d, J = 11), 5.68 (d, J = 17), 6.68 (dd, J = 11, 17), 7.1-7.9 (aromatic)
2e	CO_2Et	H	Me	H	9o	51	119-120[j,m]	3270 (NH), 1720 (ester), 1660 (NAc)	1.38 (Et, t), 2.18 (NAc, s), 4.34 (Et, q), 5.38 (d, J = 11), 5.64 (d, J = 17), 6.67 (dd, J = 11, 17)
2g	H	Me	Me	H	9p	63	135-136[k]	3260 (NH), 1655 (NAc)	2.12 (NAc, s), 2.30 (Me, s), 5.25 (d, J = 10), 5.55 (d, J = 17), 6.73 (dd, J = 10, 17), 6.9-7.5 (aromatic)

[a] Satisfactory analytical data for C, H, and N (±0.4%) were obtained for new compounds. [b] Lit.[20] mp 140 °C. [c] From chloroform. [d] From ethanol. [e] From benzene. [f] Lit.[21] mp 172-174 °C. [g] Accompanied by quinoline (38%). [h] From benzene-ethanol. [i] From chloroform-ethanol. [j] From benzene-hexane. [k] From benzene-cyclohexane. [l] Lit.[8] mp 96-98 °C. [m] Lit.[8] mp 121-122 °C. [n] From cyclohexane; lit.[8] mp 94.5 °C.

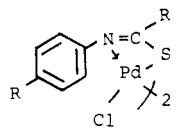
Scheme I



esters **4b–j** (Table I). Formation of 4-substituted *N*-acetylanthranilates **4g–j** from meta-substituted acetanilides shows that the metalation had occurred at the ortho position of the unsubstituted site, i.e., the 6-position of the aromatic ring of **1g–j**.

o-Chloroacetanilide, *o*-methylacetanilide, and *o*-methoxyacetanilide did not react with $Pd(OAc)_2$ under our conditions. *N*-Acetyl-naphthylamine reacted easily with $Pd(OAc)_2$ to produce an unidentified complex and considerable palladium black, whereas *N*-acetyl-α-naphthylamine was recovered under the same conditions. Interference with the metalation by an ortho substituent of an acetanilide suggests that coordination of palladium with the amide nitrogen may be an important factor. Fur-

thermore, it appears that the amide group must be able to assume its tautomeric form, because *N*-methylacetanilide did not undergo ortho palladation with $PdCl_2$[11] nor with $Pd(OAc)_2$ under our conditions. Recently, formation of complex **7** has been reported instead of the ortho-palladation complex in the reaction of thioacetanilide with Na_2PdCl_4.[13]



7

Reactions of propion- (**1k**), isobutyr- (**1l**), and pivalanilides (**1m**) with $Pd(OAc)_2$ produced the corresponding complexes **2k**, **2l**, and **2m**. These were converted to the anthranilic esters **4k**, **4l**, and **4m** by carbonylation, and **2k** was converted to the pyridine complex **3k**. On the contrary, neither acrylanilide (**1n**) nor benzanilide (**1o**) gave any complex even under more drastic conditions. Since the acyl groups of **1n** and **1o** are more electronegative than those of the saturated amides, the electron density of the amide nitrogen, and consequently its ability to coordinate, may be reduced.

Reactions of **2a–m** with various olefins in the presence of triethylamine were carried out by the procedure previously reported.[6] Olefins coupled selectively at the palladium-bearing carbon of **2a–m** to give the 2-substituted vinylacetanilides shown in Table II. Acrolein diethyl acetal reacted with **2a** to give the aldehyde **8e** together with quinoline, which may have been formed by acidic components on the silica gel column used for purification. Because of fairly good yield of **8g**, coupling reactions of the other complexes **2b–j,k,m** with methyl vinyl ketone were carried out. The reactions of **2a–g** with ethylene in the presence of Et_3N gave 2-vinylacetanilide (**9k**) and its derivatives **9l–p**, as shown in Table II.

Acid-catalyzed cyclization of *o*-aminocinnamic acid has been reported to produce carbostyril.[14] In addition, reduction of (α-methyl-*o*-nitrobenzylidene)acetone in the presence of zinc and HCl has given a quinaldine derivative.[15] In an analogous fashion, treatment of **8e–g** with boiling HCl quickly produced quinoline, carbostyril, and quinaldine, respectively.

Experimental Section

The metalations were carried out in Schlenk flasks under nitrogen. Toluene was distilled and stored under a nitrogen atmosphere. The other reactions were run in air. Infrared spectra were measured on a Hitachi 215 spectrometer by using KBr pellets. Absorptions are reported in reciprocal centimeters. NMR spectra were measured on a Hitachi R-22 spectrometer. Chemical shifts are reported as δ values relative to Me_4Si as the internal standards, and the coupling constants in parentheses are recorded in hertz. Deuteriochloroform was used as the solvent unless stated otherwise. Melting points were determined in open capillaries and are uncorrected. Palladium acetate was made according to the reported procedure.[16]

Di-μ-acetato-bis(2-acetaminophenyl-*2C,O*)dipalladium(II) (2a). Into a mixture of **1a** (4.05 g, 30 mmol) and $Pd(OAc)_2$ (3.23 g, 14.4 mmol) was added toluene (50 mL), and the solution was refluxed under a slow stream of nitrogen for 30 min. The precipitate from the solution was quickly filtered and washed with fresh solvent to give greenish yellow **2a:** 2.10 g; dec 210–213 °C. The filtrate was again refluxed for 90 min, and the deposited **2a** (1.24 g; dec 204–205 °C) was collected. Further refluxing of the filtrate from the second reaction yielded a third crop of **2a**: 0.95 g; dec 205–206 °C (total yield of **2a** was 4.29 g, 99.3% based on palladium). The final mother liquor of the reaction was concentrated under reduced pressure to give recovered **1a**: 1.80 g; IR 3290 (NH), 1625, 1570 (NAc); NMR (Me_2SO-d_6) 1.35 and 2.28 (OAc, bridged and monodentate, s), 1.90 (NAc, s), 6.60–7.10 (aromatic), 11.2 (NH). Anal. Calcd for $(C_{10}H_{11}O_3NPd)_2$: C, 40.05; H, 3.70; N, 4.67. Found: C, 40.18; H, 4.24; N, 5.25.

Pyridine Derivative 3a. Pyridine (0.4 mL) was added to a suspension of **2a** (200 mg, 0.34 mmol) in benzene (6 mL). Stirring the mixture at 80 °C gave immediately a colorless powder, **3a** (251 mg, 0.66 mmol, 97%). Recrystallization from ethanol gave the analytical sample: dec 181 °C; IR 3270 (NH), 1605 and 1585 (NAc), 1580 and 1385 (OAc) cm^{-1}; NMR (Me_2SO-d_6) 1.84 (NAc, s), 2.25 (OAc, s), 6.65–7.10 (aromatic), 7.50–8.62 (pyridine). Anal. Calcd for $C_{15}H_{16}O_3N_2Pd$: C, 47.53; H, 4.26; N, 7.39. Found: C, 47.23; H, 4.59; N, 6.92.

The reactions of the other amides with $Pd(OAc)_2$ and preparation of their pyridine complexes were carried out in the same way.

Di-μ-chloro-bis(2-acetaminophenyl-*2C,O*)dipalladium(II) (5a). A mixture of **2a** (300 mg, 0.5 mmol) and LiCl (100 mg, 2.4 mmol) was stirred in a mixture of acetone (10 mL) and water (1 mL) for 2 h. The yellow solution was concentrated in vacuo. The residue was washed with water and dried to produce a greenish yellow complex, **5a**: 245 mg, (72%); dec 195 °C (recrystallized from CH_3CN); IR 3340 (NH), 1595 and 1540 (NAc); NMR (Me_2SO-d_6) 1.93 (NAc, s), 6.67–7.70 (aromatic), 11.5 (NH). Anal. Calcd for $(C_8H_8ONClPd)_2$: C, 34.77; H, 2.92; N, 5.07. Found: C, 34.84; H, 3.02; N, 5.37.

Pyridine Derivative 5b. Compound **5a** (100 mg, 0.147 mmol) was added to a benzene solution (6 mL) of pyridine (0.2 mL). Stirring the mixture readily produced a colorless powder, which was recrystallized from benzene–EtOH to give **5b** (102 mg, 0.29 mmol, 99%). Anal. Calcd for $C_{13}H_{13}ON_2ClPd$: C, 43.92; H, 3.69; N, 7.88. Found: C, 43.91; H, 3.73; N, 7.83.

Bromination of 2a. To a suspension of **2a** (330 mg, 0.55 mmol) and NaOAc (82 mg, 1 mmol) in CH_2Cl_2 (10 mL) was added bromine (185 mg, 1.1 mmol) in a solution of CCl_4 (5 mL) during 30 min at room temperature. The reaction mixture was poured into an aqueous solution (30 mL) of Na_2SO_3 (3 mmol). After separation of $PdBr_2$, the filtrate was concentrated and then chromatographed on a silica gel column. Elution with benzene–EtOAc (10:1) afforded colorless needles [167 mg (0.78 mmol, 70%); mp 95–97 °C (lit.[17] mp 99 °C)] which were identical with authentic *o*-bromoacetanilide by comparison of the IR spectra and by the mixture melting point test.

Hydrogenation of 2a. An ethanolic solution of **2a** (150 mg, 0.25 mmol) was stirred in an atmosphere of hydrogen for 40 min. Hydrogen (14 mL) was absorbed. Separation of the deposited palladium (47 mg, 0.44 mmol) followed by evaporation of the solvent gave **1a** (60 mg, 0.44 mmol, 88%).

Reaction of 2a with Carbon Monoxide. An ethanolic solution (30 mL) of **2a** (900 mg, 1.5 mmol) was placed in a thick-walled tube fitted with a mechanical stirrer. Carbon monoxide (2 atm) was introduced, and the mixture was stirred for 60 min at room temperature. The system changed from a yellow solution to a black suspension. The reaction mixture was allowed to stand overnight. Filtration of the solvent to remove metallic palladium (262 mg, 2.46 mmol) and concentration of the filtrate gave colorless crystals of **4a**: 493 mg (2.38 mmol, 79%); mp 66–68 °C (lit.[18] mp 68 °C); IR 3250 (NH), 1710 (ester), 1685 (NAc).

Hydrolysis of **4a** with an ethanolic solution of 5% NaOH yielded *N*-acetylanthranilic acid, mp 183–184 °C (lit.[17] mp 185 °C), which was identical with an authentic sample by comparison of their IR spectra and by a mixture melting point test.

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Table III. Physical Properties of Carbonylation Products[a]

compd	mp, °C	IR (KBr), cm^{-1}	NMR ($CDCl_3$), δ (J, Hz)
4b	107-108[b,c]	3275 (NH), 1690 (ester), 1675 (NAc)	1.42 (Et, t), 2.21 (NAc, s), 4.37 (Et, q), 7.30 (dd, J = 8, 3), 7.23 (d, J = 3), 8.50 (d, J = 8)
4c	97-98[d]	3270 (NH), 1695 (ester), 1680 (NAc)	1.41 (Et, t), 2.18 (NAc, s), 3.98 (OMe, s), 4.36 (Et, q), 7.02 (dd, J = 8, J = 3), 7.23 (d, J = 3), 8.54 (d, J = 8)
4d	129[c]	3275 (NH), 1705 (ester), 1680 (NAc)	1.43 (Et, t), 2.23 (NAc, s), 4.43 (Et, q), 7.45 (dd, J = 10, 3), 7.95 (d, J = 3), 8.67 (d, J = 10)
4e	100-102[e]	3260 (NH), 1760 and 1715 (ester), 1670 (NAc)	1.42 (Et, t), 1.45 (Et, t), 2.25 (NAc, s), 4.43 (Et, q), 8.07 (dd, J = 9, 2), 8.64 (d, J = 2), 8.82 (d, J = 9)
4f	146-147[c]	3270 (NH), 1720 (Ac), 1700 (ester), 1675 (NAc)	1.45 (Et, t), 2.27 (NAc, s), 2.60 (Ac, s), 4.39 (Et, q), 4.42 (Et, q), 8.15 (dd, J = 9, J = 2), 8.70 (d, J = 2), 8.79 (d, J = 9)
4g	71-72[e]	3240 (NH), 1690 (ester), 1680 (NAc)	1.40 (Et, t), 2.20 (NAc, s), 2.37 (Me, s), 4.34 (Et, q), 6.84 (dd, J = 9, 2), 7.87 (d, J = 9), 8.49 (d, J = 2)
4h	67-68[d]	3250 (NH), 1695 (ester), 1675 (NAc)	1.38 (Et, t), 2.21 (NAc, s), 3.85 (OMe, s), 4.32 (Et, q), 6.53 (dd, J = 9, 3), 7.89 (d, J = 9), 8.33 (d, J = 3)
4i	76[c]	3260 (NH), 1680 (ester), 1660 (NAc)	1.42 (Et, t), 2.23 (NAc, s), 4.37 (Et, q), 6.99 (dd, J = 9, 2), 7.92 (d, J = 9), 8.79 (d, J = 2)
4j	113-114[d]	3260 (NH), 1715 and 1705 (ester), 1660 (NAc)	1.43 (Et, t), 2.23 (NAc, s), 3.39 (OMe, s), 4.38 (Et, q), 7.65 (dd, J = 8, 3), 8.03 (d, J = 3), 9.20 (d, J = 8)
4k	48-49[e]	3270 (NH), 1705 (ester), 1685 (NAc)	1.27 (Et, t), 1.40 (Et, t), 2.46 (Et, q), 4.44 (Et, q), 6.98 (t, J = 8), 7.45 (dt, J = 8, 2), 7.94 (dd, J = 8, 2), 8.67 (d, J = 8)
4l	120-130[f] (2 mm)	3320 (NH), 1710 (ester),[g] 1680 (NAc)	1.25 (i-Pr, d), 1.46 (Et, t), 2.52 (i-Pr, hept), 4.31 (Et, q), 6.87 (t, J = 7), 7.38 (dt, J = 7, 2), 7.81 (dd, J = 8, 2), 8.67 (d, J = 8)
4m	42-44[e]	3260 (NH), 1700 (ester), 1670 (NAc)	1.30 (t-Bu, s), 1.40 (Et, t), 4.31 (et, q), 6.88 (t, J = 8), 7.41 (dt, J = 8, 2), 7.85 (dd, J = 9, 2), 8.74 (d, J = 9)

[a] Satisfactory analytical data for C, H, and N were obtained for new compounds. [b] Lit.[19] mp 112 °C. [c] From ethanol. [d] From benzene-hexane. [e] From hexane. [f] Boiling point, bath temperature. [g] Neat.

Carbonylation of the other complexes was carried out by analogous procedures (Table I). Their spectral data are listed in Table III.

Reaction of 2a with Styrene. A toluene solution (25 mL) of Et_3N (800 mg, 7.9 mmol) and then styrene (300 mg, 2.9 mmol) were added to **2a** (1010 mg, 1.68 mmol) successively. The mixture was refluxed for 15 min. After separation of palladium (353 mg), the filtrate was concentrated under reduced pressure, and the residue was crystallized from EtOH, giving colorless crystals of **8a**: 418 mg (52.4%); mp 141–142 °C (lit.[20] mp 140 °C).

The reaction of **2a** with 3,4-(methylenedioxy)styrene or 3-acetoxy-4-methoxystyrene was carried out in the same way (Table II).

Reaction of 2a with Acrolein Diethyl Acetal. A toluene solution (7.5 mL) of **2a** (300 mg, 0.5 mmol), acrolein diethyl acetal (390 mg, 3 mmol), and Et_3N (350 mg, 3.5 mmol) was refluxed for 30 min. The reaction mixture was filtered and concentrated under reduced pressure. The resulting oil (290 mg) was chromatographed on silica gel (Wako gel C-200, 7 g). The first elution with benzene–EtOAc (10:1) gave an orange oil (50 mg, 38%) which was identified as quinoline by GLC (PEG 20M). The second fraction with the same solvent was colorless crystals of **8e**: 75 mg (40%); mp 163–164 °C. Anal. Calcd for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.31; H, 5.84; N, 7.40.

Reaction of 2a with Methyl Vinyl Ketone. A mixture containing **2a** (300 mg, 0.5 mmol), methyl vinyl ketone (300 mg, 4.3 mmol), and Et_3N (350 mg, 3.5 mmol) in toluene (7.5 mL) was refluxed for 45 min. The mixture was filtered and concentrated under reduced pressure. The residue was recrystallized from benzene to yield colorless crystals of **8g**: 168 mg (0.828 mmol, 83%); mp 126–127 °C. Anal. Calcd for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.64; H, 6.50; N, 6.90.

The reactions of **2b–j** with methyl vinyl ketone were carried out similarly to that of **2a** (Table II).

Reaction of 2a with Ethylene. A solution of Et_3N (400 mg, 4 mmol) in toluene (25 mL) was added to **2a** (300 mg, 0.5 mmol) in a Taiatsu glass TEM-U-type reactor. Ethylene at a 3-atm pressure was introduced, and the mixture was heated with stirring for 35 min. The reaction took place gradually above 50 °C, liberating palladium metal. Filtration followed by concentration of the reaction mixture yielded a yellow oil (184 mg), which was chromatographed on a silica gel. Elution with benzene–EtOAc (10:1) gave colorless needles (113 mg, 70%) of *o*-vinylacetanilide **9k**, mp 90.5–91.5 °C (recrystallized from cyclohexane) (lit.[8] mp 94.5 °C).

An ethanolic solution (20 mL) of *o*-vinylacetanilide (160 mg, 1 mmol) obtained as above was hydrogenated over 5% Pd/C to afford colorless crystals [144 mg (88%); mp 112–112.5° (lit.[17] mp 111–112 °C)] which were identified with authentic *o*-ethylacetanilide by comparison of IR spectra.

Acid-Catalyzed Cyclization of 8g. A suspension of **8g** (150 mg, 0.74 mmol) in concentrated HCl (2 mL) was refluxed for 2–3 min and then poured into water (50 mL). The mixture was neutralized with Na_2CO_3 powder and extracted with ether. The ether solution was concentrated to give an oil (93 mg) which had the same retention time as quinaldine by GLC. Treatment of the oil with picric acid (140 mg) in EtOH (20 mL) gave quinaldine picrate [193 mg (70%); mp 192 °C (lit.[17] mp 194 °C)] which was identical with an authentic sample by comparison of their IR spectra.

Treatment of **8e** and **8f** with hydrochloric acid and a subsequent work up in a similar way gave quinoline [80%; picrate, mp 199 °C (lit.[17] mp 203–204 °C)] and carbostyril [54%; mp 190 °C (lit.[17] mp 199–200 °C)], which were identical with authentic samples by comparison of their IR spectra.

Acknowledgment. We are grateful to Kawaken Fine Chemical Co. Ltd., for a gift of palladium chloride.

Registry No. 1a, 103-84-4; **1b**, 103-89-9; **1c**, 51-66-1; **1d**, 539-03-7; **1e**, 5338-44-3; **1f**, 2719-21-3; **1g**, 537-92-8; **1h**, 588-16-9; **1i**, 588-07-8; **1j**, 52189-36-3; **1k**, 620-71-3; **1l**, 4406-41-1; **1m**, 6625-74-7; **1n**, 2210-24-4; **1o**, 93-98-1; **2a**, 72573-63-8; **2b**, 72585-58-1; **2c**, 79057-65-1; **2d**, 79057-66-2; **2e**, 79057-67-3; **2f**, 79057-68-4; **2g**, 79057-69-5; **2h**, 79057-70-8; **2i**, 79057-71-9; **2j**, 79057-72-0; **2k**, 79057-73-1; **2l**, 79057-74-2; **2m**, 79057-75-3; **3a**, 72556-87-7; **3b**, 79057-76-4; **3c**, 79057-77-5; **3d**, 79057-78-6; **3e**, 79057-79-7; **3f**, 79057-80-0; **3g**, 79057-81-1; **3h**, 79057-82-2; **3i**, 79057-83-3; **3j**, 79057-84-4; **3k**, 79057-85-5; **4a**, 20628-20-0; **4b**, 63243-79-8; **4c**, 79043-88-2; **4d**, 29551-91-5; **4e**, 79043-89-3; **4f**, 79057-64-0; **4g**, 79043-90-6; **4h**, 79043-91-7; **4i**,

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Asymmetric Hydroformylation of Vinyl Acetate with DIOP-Type Ligands

Charles F. Hobbs* and W. S. Knowles

Corporate Research Laboratories, Monsanto Company, St. Louis, Missouri 63166

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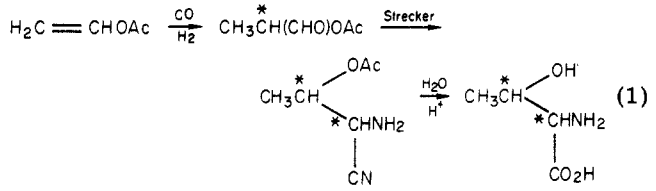
The rhodium-catalyzed hydroformylation of vinyl acetate and related esters was carried out in the presence of chiral phosphine ligands of the DIOP type to give the corresponding optically active 2-(acyloxy)propanal, a precursor for the amino acid threonine. Ligand structure and the ligand/metal ratio were the primary factors controlling asymmetric induction; temperature, CO pressure, and solvent polarity had minor effects. The highest induction efficiencies, up to 51% ee, were obtained with the 5*H*-dibenzophospholyl derivative of DIOP[7] (DIPHOL, **1e**).

The synthesis of optically active compounds by asymmetric catalysis has gene rated increasing interest in recent years. Following success in achieving high efficiencies in asymmetric hydrogenation,[1] attention has turned to applying asymmetric catalysis to other reactions such as hydroformylation.[2-5] Asymmetric hydroformylation of vinyl acetate, for example, is particularly attractive as it leads to chiral 2-acetoxypropanal, a precursor for the



(1)

Strecker synthesis of the amino acid threonine.[6] For simple hydrocarbon olefins, efficiencies of asymmetric induction for hydroformylation have been modest, with maximum enantiomeric excesses (ee) reaching about 30% with DIOP[7]-type ligands.[8-11] Higher optical yields, in the 40% range, have been reported for hydroformylation of styrene and its derivatives with DIPHOL.[12-14] Asymmetric hydroformylation of vinyl acetate has been studied[15,16], the highest optical yield reported being 32%, achieved by using DIOP.[16] In this paper, we report on the rhodium-catalyzed hydroformylation of vinyl acetate and related esters in the presence of DIOP and several new DIOP derivatives which afford improved asymmetric induction efficiencies.

Results

Hydroformylation of vinyl acetate was carried out in the presence of rhodium catalysts complexed with a series of DIOP-type ligands at various ligand-to-rhodium ratios and under a variety of pressure and temperature conditions. In general, catalyst complexes were prepared in situ from Rh(COD)acac and the desired DIOP analogue although in the case of DIOP itself and DIPHOL discreet rhodium complexes were prepared independently and charged into the reaction mixture. The effects of ligand structure and reaction variables on the reaction rate and asymmetric induction (enantiomeric excess, ee) are summarized in Table I.

The major product was 2-acetoxypropanal produced with selectivities generally in the range of 75–95%. Minor amounts of the 3-acetoxy isomer were also produced; this partly decomposed under the conditions of reaction to give acetic acid and acrolein which was hydrogenated to propanal under the conditions of the reaction.

The extent of asymmetric induction varied widely and depended primarily on the ligand structure and the lig-

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