# Binary α-Unsaturated Palladium Carboxylates and Their Complexes with Morpholine Derivatives: the Crystal Structure of Palladium Carbamoyl Crotonate (OC<sub>4</sub>H<sub>8</sub>NH)<sub>2</sub>Pd[OC<sub>4</sub>H<sub>8</sub>N(C=O)](MeCH=CHCO<sub>2</sub>) · H<sub>2</sub>O, a Product of the First Inner-Sphere Amination Reaction of α-Unsaturated Palladium Carbonyl Carboxylates with Morpholine

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Abstract—Binary  $\alpha$ -unsaturated palladium carboxylates have been synthesized by substitution of  $\alpha$ -unsaturated acids RCOOH (R is CH<sub>2</sub>=C(Me), MeCH=CH, PhCH=CH) for the acetate ion in Pd<sub>3</sub>(µ-MeCOO)<sub>6</sub>. These carboxylates react with amines A (A is morpholine (M), methylmorpholine (MM), or thiomorpholine (MS)) to give *trans*-Pd(A)<sub>2</sub>(RCOO)<sub>2</sub> similar to *trans*-A<sub>2</sub>(MeCO<sub>2</sub>)<sub>2</sub>. The structures of the *trans*-Pd(A)<sub>2</sub>(RCOO)<sub>2</sub> complexes (R is MeCH=CH; A is M, MM, MS) have been determined by X-ray crystallog-raphy. The effect of solvent on the crystal structure of the complexes has been demonstrated for *trans*-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NO)<sub>2</sub> as an example. The amination reaction of palladium carbonyl crotonate with a secondary amine, morpholine, has been studied for the first time. The reaction involves disproportion-ation of Pd(I) into Pd(0) and Pd(II) and leads to the first unsaturated palladium(II) carbamoyl carboxylate—palladium carbamoyl crotonate *trans*-(OC<sub>4</sub>H<sub>8</sub>NH)<sub>2</sub>Pd[OC<sub>4</sub>H8NC(=O)](MeCH=CHCO<sub>2</sub>) · H<sub>2</sub>O, as well as to *trans*-M<sub>2</sub>Pd(MeCH=CHCO<sub>2</sub>)<sub>2</sub> and (C<sub>4</sub>H<sub>10</sub>NO)<sup>+</sup>(MeCH=CHCO<sub>2</sub>)<sup>-</sup>. The structures of these compounds have been proved by X-ray crystallography.

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At present, palladium carboxylates attract attention of coordination chemists because of revealing new trends and properties in a series of aliphatic palladium complexes [1], as well as due to their practical application as catalysts (or their precursors) of organic reactions [2–7]. In the chemistry of platinum metals, a few unsaturated carboxylates containing double and triple bonds in the carboxylate ligand have been described: heterometallic Os and Ru complexes with acetylcarboxylic acid [8], platinum heterocarboxylate complex  $Pt_4(MeCO_2)(CH=CHCO_2)_4$  [9], and polynuclear ruthenium complexes with unsaturated acids [10].

As for unsaturated palladium carboxylates, only five structurally characterized compounds with such anions are known: the mononuclear  $(P'Pr_3)_2Pd(MeCH=C(CH_2CH=CH-CH=CH_2)CO_2)_2$  [11] and  $(dppf)Pd(cis-HO_2CCH=CHCO_2)_2$  [12] complexes, the polymeric {[dppf)Pd(RCO\_2]]+CF\_3SO\_3}<sub>n</sub> complex (dppf is 1,1'-bis(diphenylphosphino)fer-

 $(PPh_3)_2Pd(\mu$ rocene) [13], the binuclear  $CH_2 = C(Me)CH_2CO_2)(\mu - CH_2 = C(Me)CH_2)Pd$  (PPh<sub>2</sub>) complex [14], and the only binary cyclic palladium tiglate Pd<sub>3</sub>MeCH=CH(Me)CO<sub>2</sub>)<sub>6</sub> [15]. Recently, we have described the synthesis and spectral characteristics of palladium carbonyl and nitrosyl carboxylates and have synthesized palladium carbonyl and nitrosyl carboxylates  $Pd_4(\mu-CO)_4(\mu-RCO_2)_4$  and  $Pd_4(\mu-NO)_2(\mu-RCO_2)_6$ , where  $\mathbf{R} =$ trans-MeCH=C(Me) [16],  $CH_2 = CH$ ,  $CH_2 = C(Me),$ trans-MeCH=CH, PhH=CH, and trans-MeCH=C(Me). The structures of the  $Pd_4(\mu$ - $CO_4(\mu-MeCH=CHCO_2)_4$  and  $Pd_4(\mu-NO)_2(\mu-MeCH=CHCO_2)_4$  $CH_2 = CH(Me)CO_2)_6$  complexes have been proved by X-ray crystallography [17]. No information is available on unsaturated palladium carboxylates with nitrogen-containing ligands.

In the present paper, we report the synthesis of binary  $\alpha$ -unsaturated palladium carboxylates and the results of studying the reactions of secondary

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amines—morpholine derivatives—with both binary palladium carboxylates and palladium carbonyl crotonate. The latter reaction has led, for the first time, to  $\alpha$ -unsaturated palladium carbamoyl carboxylate, a product of amination of the coordinated CO molecule in palladium carbonyl crotonate.

## EXPERIMENTAL

Initial compounds and methods of investigation. The following reagents were used: 98% cinnamic acid, 98% crotonic acid, 99.5% acrylic and methacrylic acids, morpholine  $C_4H_9NO$ , 4-methylmorpholine  $C_5H_{11}NO$ , and thiomorpholine  $C_4H_9NS$  (ACROS Organics); NaOH (pure for analysis); CHCl<sub>3</sub>, benzene, toluene, diethyl ether, hexane, petroleum ether, and methylene chloride; acetic, nitric, and formic acids (all chemically pure, Khimmed).

Palladium complexes with acids were synthesized from palladium acetate  $Pd_3(\mu-MeCO_2)_6(1)$  obtained by our new original method, palladium tiglate  $Pd_3(\mu-MeCO_2)_6$  synthesized as described in [15], and palladium carbonyl crotonate synthesized as described in [17].

Analysis for C, H, N was carried out on a Carlo Erba Instruments CHNS OEA 1108 analyzer.

Single-crystal X-ray diffraction analysis of compounds was carried out on a Bruker SMART APEX II automated diffractometer (Mo $K_{\alpha}$  radiation,  $\lambda =$ 0.71073 Å, graphite monochromator,  $\omega$  scan). The structures were solved by direct methods and refined anisotropically by full-matrix least-squares calculations on  $F^2$  for all non-hydrogen atoms (SHELXTL-Plus). All hydrogen atoms in structure 12 were located from a difference Fourier synthesis and refined isotropically; in structures 10 and 17, all hydrogen atoms were introduced in calculated positions and refined as riding on their parent atoms. In structures 8, 8a, 16, and 18, the H atoms bonded to the carbon atoms were placed in calculated positions and refined as riding of these atoms, while the amine hydrogen atoms were located from electron density maps and refined isotropically. The crystal characteristics and experimental and refinement details are summarized in Table 1. The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC 1043133-1043139).

Powder X-ray diffraction analysis was carried out on a Bruker D8 ADVANCE diffractometer (Cu $K_{\alpha}$  radiation, Ni filter, LynxEye detector) of the Shared Facility Center at the Institute of General and Inorganic Chemistry, RAS.

The IR absorption spectra of the compounds in the range 4000-225 cm<sup>-1</sup> were recorded on a Nicolet NEXUS IR FT spectrophotometer. Samples were ground with mineral oil. The resulting mulls were placed between KRS-5 plates.

The multiple attenuated total reflectance (MATR) IR spectra of the complexes in the range 4000–

550 cm<sup>-1</sup> were recorded on a Nicolet NEXUS IR FT spectrophotometer equipped with a Pike diamond ATR sampling accessory. The samples were applied to a diamond crystal without additional preparation. This sampling procedure made it possible to avoid side processes initiated by grinding the samples with mineral oil and by compacting the samples into pellets with KBr.

The Raman spectra of the complexes were recorded on a LabRAM-300 laser spectrophotometer (He–Ne laser excitation at 632.8 nm with a power of no more than 0.3 mW to avoid sample degradation).

# Synthesis of Binary Palladium Carboxylates

New method of synthesis of  $Pd_3(\mu-MeCO_2)_6$  (1). In a 1000-mL heat-resistant glass beaker, 14 g of  $(NH_3)_4PdC_{14}$  was dissolved in 250 mL of distilled water; then, 350 mL of formic acid was added, and the reaction mixture was refluxed for 2 h until the formation of palladium black (sponge) in a transparent colorless solution. The solution was carefully decanted, and palladium black was washed in the same beaker with water  $(7 \times 500 \text{ mL})$  to remove chlorine traces (AgNO<sub>3</sub> test) and, then, with acetic acid ( $2 \times 200 \text{ mL}$ ). The activated black with a small amount of acetic acid was placed into a 1000-mL two-neck round-bottom flask; then, 300 mL of acetic acid and 1.5 mL of HNO<sub>3</sub> were added, and the mixture was refluxed for 4 h until complete disappearance of brown nitrogen oxides. The hot orange brown solution was filtered through a Schott filter (no. 40) to remove the unreacted palladium metal; the solution was concentrated in a rotary evaporator to 25 mL and cooled until a crystalline precipitate formed. The resulting orange precipitate was filtered off through a Schott filter (no. 40) and dried first in air with the use of a water-jet pump for 1 h and then in a vacuum at 93 Pa for 2 h to constant weight. The product was an orange crystalline powder. The yield was 6.24 g (45% based on the introduced palladium).

The contents of C, H, and N in  $C_4H_6O_4Pd$  determined in samples of five independent syntheses carried out in analytical laboratories at (a) the Institute of General and Inorganic Chemistry, RAS, and (b) the Institute of Organic Chemistry, RAS, are summarized in Table 2.

The elemental analysis data for these samples confirm the synthesis of pure palladium acetate (Table 2).

IR (cm<sup>-1</sup>): 1594 s,  $v_{as}$ (COO); 1415 s,  $v_{s}$ (COO).

 $Pd_3(\mu$ -CH<sub>2</sub>=C(Me)CO<sub>2</sub>)<sub>6</sub> (3). A 1.5-fold excess (as calculated for palladium) of methacrylic (2-methylacrylic) acid (254 mL, 3 mmol) was introduced into a solution of 224 mg (1 mmol) of Pd<sub>3</sub>(MeCO<sub>2</sub>)<sub>6</sub> in 30 mL of toluene under stirring and heating (45– 50°C). The color of the reaction mixture changed to dark orange are remained unaltered for 2 h. Then, the solution was filtered from the palladium metal through

	1	1					
	8	8a	10	12	16	17	18
Empirical formula	$\mathrm{C}_{16}\mathrm{H}_{28}\mathrm{N}_{2}\mathrm{O}_{6}\mathrm{Pd}$	$\mathrm{C}_{16}\mathrm{H}_{28}\mathrm{N}_{2}\mathrm{O}_{6}\mathrm{Pd}$	$\mathrm{C}_{18}\mathrm{H}_{32}\mathrm{N}_{2}\mathrm{O}_{6}\mathrm{Pd}$	$C_{16}H_{28}N_2O_4PdS_2$	$C_{17}H_{33}N_3O_7Pd$	$C_8H_{15}NO_3$	$C_8H_{15}NO_2S$
FW	450.80	450.80	478.86	482.92	497.86	173.21	189.27
Crystal size, mm	$0.38\times0.06\times0.02$	$0.35 \times 0.25 \times 0.20$	$0.13\times0.12\times0.05$	$0.35\times0.25\times0.20$	$0.30\times0.20\times0.20$	$0.40\times0.05\times0.05$	$0.25\times0.20\times0.20$
T, K	183	150	153	183	150	150	150
Symmetry system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	Pccn	$P\overline{1}$	$P2_{1/c}$	$P2_1/n$	$P2_{1/c}$	Pc
Unit cell parameters							
$a,  m \AA$	7.3588(9)	12.9630(8)	7.046(10)	10.3362(12)	10.4914(5)	5.6761(9)	5.6503(5)
$b, { m \AA}$	8.7751(11)	19.2224(12)	8.207(12)	12.8027(15)	10.9972(5)	16.696(3)	33.581(3)
$c,  m \AA$	14.4640(17)	7.4581(5)	9.449(14)	8.1359(9)	19.5684(9)	10.1470(16)	11.1524(10)
$\alpha$ ,deg	06	06	71.674(19)	90	90	90	90
$\beta$ , deg	92.462(2)	06	88.56(2)	110.629(2)	104.072(1)	100.812(2)	99.786(1)
$\gamma$ , deg	06	06	77.24(2)	90	90.00	06	90
$V, Å^3$	933.1(2)	1858.4(2)	505.3(13)	1007.6(2)	2189.97(18)	944.5(3)	2085.3(3)
Ζ	2	4	1	2	4	4	8
$\rho_{calc}, g/cm^3$	1.604	1.611	1.574	1.592	1.510	1.218	1.206
$\mu(MoK_{\alpha}), mm^{-1}$	1.028	1.032	0.954	1.150	0.888	0.093	0.275
F(000)	464	928	248	496	1032	376	816
$\theta$ range, deg	2.72-28.00	2.12 - 28.00	2.92-29.50	2.64 - 28.00	2.15 - 26.00	2.38 - 25.05	2.61 - 26.00
Total number of reflections	9329	14601	4953	8963	15819	6163	15179
Number of unique reflections $(R_{int})$	2251 (0.0260)	2231 (0.0329)	2665 (0.0454)	2407 (0.0247)	4268 (0.0302)	1654 (0.0256)	7956 (0.0387)
Number of variables	116	121	126	171	268	110	469
$R_1$ for $I > 2\sigma(I)$	0.0240	0.0257	0.0637	0.0198	0.0241	0.1114	0.0485
$wR_2$ (all data)	0.0671	0.0697	0.2061	0.0505	0.0608	0.2504	0.1160
GOOF on $F^2$	1.057	1.067	1.130	1.025	1.061	1.188	0.965
Flack parameter	Ι	Ι	I	I	I	I	-0.04(6)
$\Delta \rho_{min}/\Delta \rho_{max}, e/Å^3$	-0.278/0.726	-0.417/0.624	-2.256/1.624	-0.472/0.400	-0.424/0.472	-0.495/0.899	-0.248/0.286

Table 1. Crystal data and experimental details for complexes 8, 8a, 10, 12, 16, 17, and 18

	C	<b>`</b> *	Н	**	1	Ν
Sample no.	foun	d, %	foun	id, %	foun	id, %
	а	b	а	b	а	b
1	21.24	21.23	2.69	2.87	0.00	0.00
2	21.29	21.14	2.63	2.84	0.00	0.00
3	21.29	21.21	2.90	2.87	0.00	0.00
4	21.39	21.19	2.75	2.92	0.00	0.00
5	21.53	21.30	2.49	2.58	0.00	0.00

**Table 2.** Analytical characteristics of  $Pd_3(\mu-MeCO_2)_6$  samples

\* Calculated 21.39%.

\*\* Calculated 2.69%.

a Schott filter (no. 40). The filtrate was concentrated in a rotary evaporator to 5 mL. To the resulting viscous oil, diethyl ether (5 mL), hexane (10 mL), and methylene chloride (5 mL) were successively added, and the newly formed orange solution was concentrated in a rotary evaporator. To the resulting brown oil, 10 mL of methylene chloride and 10 mL of hexane were added, and the solution was concentrated in a rotary evaporator to 5 mL; then, 20 mL of hexane was added, and the solution was concentrated again until an orange crystalline precipitate formed. The resulting orange powder was recrystallized from acetone with the addition of hexane to remove possible impurities of the unreacted acid and was dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of an orange powder was 166 mg (60% based on the introduced palladium).

For C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>Pd anal. calcd. (%): C, 34.71; H, 3.62. Found (%): C, 34.33; H, 3.55.

Raman (cm<sup>-1</sup>): 1643, v(C=C).

IR (cm<sup>-1</sup>): 1643, v(C=C); 1574,  $v_{as}$ (COO); 1407,  $v_s$ (COO).

 $Pd_3(\mu-MeCH=CHCO_2)_6$  (4). A 1.5-fold excess (as calculated for palladium) of crotonic (trans-2butenoic) acid (258 mg, 3 mmol) was poured into a solution of Pd<sub>3</sub>(MeCO<sub>2</sub>)<sub>6</sub> (224 mg, 1 mmol) in 30 mL of toluene under stirring and heating to 45–50°C. The color of the reaction mixture changed to dark orange and remained unaltered for 2 h. Then, the solution was filtered from the palladium metal through a Schott filter (no. 40). The filtrate was concentrated in a rotary evaporator until the formation of 5 mL of a dark brown viscous oil; then, 5 mL of diethyl ether (for dissolving the unreacted acid residues) and 10 mL of hexane were added. The mother liquor was decanted from the deposited orange precipitate, which was washed with hexane  $(2 \times 10 \text{ mL})$  and dried in a vacuum at 93 Pa for 2 h to constant weight. The product—a light orange powder-was recrystallized from acetone with the addition of hexane to remove possible impurities of the unreacted acid and was dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the resulting orange powder was 180 mg (65% based on the introduced palladium).

For  $C_8H_{10}O_4Pd$  anal. calcd. (%): C, 34.71; H, 3.62.

Found (%): C, 34.51; H, 3.37.

Raman (cm<sup>-1</sup>): 1653, v(C=C)).

IR (cm<sup>-1</sup>): 1652, v(C=C); 1568,  $v_{as}$ (COO); 1406,  $v_s$ (COO).

 $Pd_3(\mu-PhCH=CHCO_2)_6$  (5). A sixfold excess (as calculated for palladium) of cinnamic (trans-3-phenylpropenoic) acid (1332 mg, 9 mmol) was gradually added to a solution of Pd<sub>3</sub>(MeCO<sub>2</sub>)<sub>6</sub> (224 mg, 1 mmol) in 30 mL of toluene under stirring and heating to 45-65°C. The color of the reaction mixture changed to dark orange. The synthesis was carried for 2 to 72 h. The resulting solution was filtered through a Schott filter (no. 40) from palladium metal. The filtrate was concentrated in a rotary evaporator until the formation of 5 mL of dark brown viscous oil, to which 5 mL of diethyl ether and then 10 mL of hexane were added. The mother liquor was decanted from the resulting light orange precipitate, which was washed with hexane  $(2 \times 10 \text{ mL})$  and dried in a vacuum at 93 Pa to constant weight. To remove an unreacted acid excess, the product (a light orange powder) was recrystallized two to five times from acetone with the addition of hexane and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—an orange powder-was 50 mg (13% based on the introduced palladium).

For  $C_{18}H_{14}O_4Pd$  anal. calcd. (%): C, 53.94; H, 3.50.

Found (%): C, 52.09; H, 3.60.

Raman (cm<sup>-1</sup>): 1635, v(C=C).

IR (cm<sup>-1</sup>): 1632, v(C=C); 1570,  $v_{as}$ (COO); 1389,  $v_s$ (COO).

 $Pd_3(\mu-(Me)CH=CH(Me)CO_2)_6$  (6). The synthesis was described elsewhere [15].

*trans*-(CH<sub>2</sub>=C(Me)CO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NO)<sub>2</sub> (7). Morpholine (173 mL, 2 mmol) was introduced into a solution of palladium methacrylate (276 mg, 1 mmol) in

30 mL of toluene under stirring. This induced a change in the solution color from orange to green-yellow, which did not change within 1 h of synthesis. The solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator until dry. The yellow precipitate was washed with hexane ( $2 \times 10$  mL) and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a yellow-green powder—was 382 mg (85% based on the introduced palladium).

For  $C_{16}H_{28}N_2O_6Pd$  anal. calcd. (%): C, 42.67; H, 6.22; N, 6.22.

Found (%): C, 42.98; H, 6.54; N, 6.36.

Raman (cm<sup>-1</sup>): 1640, v(C=C).

IR (cm<sup>-1</sup>): 1641, v(C=C); 1568,  $v_{as}$ (COO); 1354,  $v_s$ (COO).

*trans*-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NO)<sub>2</sub> (8). Morpholine (173 mL, 2 mmol) was introduced into a solution of palladium crotonate Pd<sub>3</sub>( $\mu$ -CH<sub>3</sub>CH=CHCO<sub>2</sub>)<sub>6</sub> (276 mg, 1 mmol) in 30 mL of toluene under stirring. This induced a change in the solution color to yelloworange, which did not change within 1 h of synthesis. The solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator until dry. The yellow precipitate was washed with hexane (2 × 10 mL) and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a yellow-green powder—was 338 mg (75% based on the introduced palladium).

For  $C_{16}H_{28}N_2O_6Pd$  anal. calcd. (%): C, 42.67; H, 6.22; N, 6.22.

Found (%): C, 42.21; H, 6.98; N, 6.41.

Raman (cm<sup>-1</sup>): 1654, v(C=C).

IR (cm<sup>-1</sup>): 1656, v(C=C); 1582, v<sub>as</sub>(COO); 1348, v<sub>s</sub>(COO); 3209, 3259, v(NH).

Single crystals of **8** for X-ray crystallography were obtained by keeping a solution of the complex in 15 mL of benzene with the addition of 5 mL of hexane at room temperature for three days.

*trans*-(PhCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NO)<sub>2</sub> (9). Morpholine (173 mL, 2 mmol) was added under stirring to a solution of palladium cinnamate  $Pd_3(\mu$ -PhCH=CHCO<sub>2</sub>)<sub>6</sub> (400 mg, 1 mmol) in 30 mL of toluene, which was accompanied by a change in color to yellow. The reaction gave a yellow precipitate, which was collected on a Schott filter (no. 16), washed with 5 mL of toluene and 5 mL of petroleum ether, and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a light yellow powder—was 258 mg (45% based on the introduced palladium).

For  $C_{26}H_{32}N_2O_6Pd$  anal. calcd. (%): C, 54.35; H, 5.57; N, 4.88.

Found (%): C, 54.37; H, 5.33; N, 4.93. Raman (cm<sup>-1</sup>): 1638,v(C=C). IR (cm<sup>-1</sup>): 1636, v(C=C); 1588  $v_{as}$ (COO); 1352,  $v_s$ (COO).

trans-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>5</sub>H<sub>11</sub>NO)<sub>2</sub> (10). 4-Methylmorpholine (220 mL, 2 mmol) was introduced into a solution of palladium crotonate  $Pd_3(\mu$ - $MeCH=CHCO_{2}$  (276 mg, 1 mmol) in 30 mL of toluene under stirring. The solution color did not change over a period of 1 h. The solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator to 5 mL. Then, 10 mL of hexane was added, and a precipitate was separated from the mother liquor by decantation. The resulting green precipitate was washed with hexane  $(2 \times 10 \text{ mL})$ and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product-a green powder-was 310 mg (65% based on the introduced palladium).

For  $C_{18}H_{32}N_2O_6Pd$  anal calcd. (%): C, 45.19; H, 6.69; N, 5.86.

Found (%): C, 45.29; H, 6.91; N, 6.07.

Raman (cm<sup>-1</sup>): 1659, v(C=C).

IR (cm<sup>-1</sup>): 1656, v(C=C); 1600,  $v_{as}$ (COO); 1336,  $v_s$ (COO).

Single crystals of **10** suitable for X-ray crystallography were obtained by keeping a solution of the complex in a mixture of 15 mL of benzene with 5 mL of hexane at room temperature for three days.

trans-(PhCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>5</sub>H<sub>11</sub>NO)<sub>2</sub> (11). 4-Methylmorpholine (220 mL, 2 mmol) was introduced under stirring into a solution of palladium cinnamate (400 mg, 1 mmol) in 30 mL of toluene. This induced a change in the solution color to yellowgreen, which did not change within 1 h of synthesis. The solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator to 5 mL. Then, 10 mL of hexane was added, which led to the formation of a green precipitate. The latter was separated from the mother liquor by decantation. The resulting green precipitate was washed with hexane  $(2 \times 10 \text{ mL})$  and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a green powder—was 291 mg (65% based on the introduced palladium).

For  $C_{28}H_{36}N_2O_6Pd$  anal. calcd. (%): C, 55.81; H, 5.98; N, 4.65.

Found (%): C, 55.95; H, 6.33; N, 4.93.

Raman (cm<sup>-1</sup>): 1639, v(C=C).

IR (cm<sup>-1</sup>): 1636,  $\nu$ (C=C); 1576,  $\nu$ <sub>as</sub>(COO); 1336,  $\nu$ <sub>s</sub>(COO).

*trans*-(CH<sub>2</sub>=C(Me)CO<sub>2</sub>)<sub>2</sub>Pd(C<sub>5</sub>H<sub>11</sub>NO)<sub>2</sub> (12). 4-Methylmorpholine (220 mL, 2 mmol) was introduced under stirring into a solution of palladium methacrylate (276 mg, 1 mmol) in 30 mL of toluene. This induced a change in the solution color to brown, which did not change within 2 h of synthesis. Then, the solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator until dry. The resulting green precipitate was washed with hexane  $(2 \times 10 \text{ mL})$  and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a green powder—was 334 mg (70% based on the introduced palladium).

For  $C_{18}H_{32}N_2O_6Pd$  anal. calcd. (%): C, 45.19; H, 6.69; N, 5.86.

Found (%): C, 44.84: H, 7.00; N, 6.00.

Raman (cm<sup>-1</sup>): 1641, v(C=C).

IR (cm<sup>-1</sup>): 1641, v(C=C); 1592, v<sub>as</sub>(COO); 1328, v<sub>s</sub>(COO).

*trans*-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NS)<sub>2</sub> (13). Thiomorpholine (201 mL, 2 mmol) was introduced under stirring into a solution of palladium crotonate Pd<sub>3</sub>( $\mu$ -MeCH=CHCO<sub>2</sub>)<sub>6</sub> (276 mg, 1 mmol) in 30 mL of benzene. This induced a change in the solution color to yellow, which did not change within 1 h of synthesis. Then, the solution was filtered through a Schott filter (no. 40) from palladium metal and concentrated in a rotary evaporator until dry. The resulting yellow precipitate was washed with hexane (2 × 10 mL) and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a yellow powder—was 409 mg (85% based on the introduced palladium).

For  $C_{16}H_{28}N_2S_2O_4Pd$  anal. calcd. (%): C, 39.80; H, 5.80; N, 5.80; S, 13.30.

Found (%): C, 39.40; H, 5.88; N, 6.00; S, 13.50. Raman (cm<sup>-1</sup>): v(C=C) 1651.

IR (cm<sup>-1</sup>): v(C=C) 1661;  $v_{as}(COO)$  1568,  $v_s(COO)$  1343, v(Pd-N) 296.

Single crystals of **13** suitable for X-ray crystallography were obtained by keeping a solution of the complex in a mixture of 15 mL of benzene with 5 mL of hexane at room temperature for three days.

[(MeCH=CHCO<sub>2</sub>)Pd( $\mu$ -C<sub>4</sub>H<sub>9</sub>NS)]<sub>2</sub> (14). Thiomorpholine (101 mL, 1 mmol) was introduced under stirring into a solution of palladium crotonate Pd<sub>3</sub>( $\mu$ -MeCH=CHCO<sub>2</sub>)<sub>6</sub> (276 mg, 1 mmol) in 30 mL of benzene, which led to the change and color and formation of a yellow precipitate. The reaction mixture was allowed to stand for 1 h until the precipitation was complete. The precipitate was filtered off through a Schott filter (no. 16), washed with toluene (2 × 10 mL) and petroleum ether (bp = 40–60°C), and dried in a vacuum at 93 Pa for 2 h to constant weight. The yield of the final product—a yellow powder—was 208 mg (55% based on the introduced palladium).

For  $C_{12}H_{19}NSO_4Pd$  anal. calcd. (%): C, 38.00; H, 5.01; N, 3.60; S, 8.40.

Found (%): C, 38.00; H, 5.02; N, 3.77; S, 8.53. Raman (cm<sup>-1</sup>): 1660, v(C=C).

IR (cm<sup>-1</sup>): 1660, v(C=C); 1570, v<sub>as</sub>(COO); 1345, v<sub>s</sub>(COO); 290, v(Pd–N); 344, v(Pd–S).

*trans*- $(OC_4H_8NH)_2Pd[OC_4H_8NC(=O)](MeCH=CHCO_2) \cdot H_2O$  (16). Morpholine (173 mL, 2 mmol) was added under stirring to a solution of palladium

carbonyl crotonate (219 mg, 1 mmol) in 20 mL of toluene. The yellow-orange color of the reaction mixture changed, which was accompanied by deposition of palladium black for 1 h. then, the solution was cooled to 4°C and filtered through a Schott filter (no. 40) from palladium metal. To the resulting pale green filtrate, 5 mL of hexane was added, and the solution was allowed to stand at 4°C for 14 days. Crystals of palladium carbamoyl crotonate **16** and morpholonium crotonate **17** were formed. After these crystals were isolated, 10 mL of methylene chloride was added to the mother liquor, which was allowed to stand at 4°C for three days for crystallization. This led to the formation of crystals of the aminate complex *trans*-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>9</sub>NO)<sub>2</sub> (**8a**).

Spectra data for palladium carbamoyl crotonate (16). Raman (cm<sup>-1</sup>): 1659, v(C=C)).

IR (cm<sup>-1</sup>): 1576, v(CO) (carbamoyl moiety); 1657, v(C=C); 1543,  $v_{as}$ (COO); 1345,  $v_s$ (COO); 3031, v(CH=); 3171, v(NH); 3402, v(H<sub>2</sub>O)).

Spectral data for morpholonium crotonate  $(C_4H_{10}NO)^+(MeCH=CHCOO)^-$  (17.

IR (cm<sup>-1</sup>): 1656, v(C=C); 1516,  $v_{as}$ (COO); 1375,  $v_s$ (COO).

Spectral data for 8a.

Raman (cm<sup>-1</sup>): 1654, v(C=C).

IR (cm<sup>-1</sup>): 1656, v(C=C); 1580,  $v_{as}$ (COO); 1348,  $v_s$ (COO); 3181, v(NH)).

In the reaction of carbonyl crotonate with thiomorpholine, analogous to the reaction with morpholine, palladium carbonyl crotonate was completely reduced to Pd(0). Only crystals of thiomorpholonium crotonate  $(C_4H_{10}NS)^+(MeCH=CHCOO)^-$  (18) were isolated from the mother liquor; the structure of 18 was also confirmed by X-ray crystallography.

#### **RESULTS AND DISCUSSION**

Among binary palladium carboxylates, aliphatic palladium carboxylates and especially  $Pd_3(\mu-CH_3CO_2)_6$  (1) are most studied [1]. As for binary palladium complexes with unsaturated acids, almost no information on their synthesis and properties is available, although it is evident that studying catalytic processes involving unsaturated organic molecules requires knowing their transformations in the presence of palladium.

Binary palladium complexes with unsaturated carboxylic acids that have the  $pK_a$ 's in the range of  $pK_a$ 's of aliphatic acids with electron-releasing substituents have been synthesized and studied: cinnamic ( $\beta$ -phenylacrylic) acid *trans*-(Ph)CH=CHCOOH ( $pK_a = 4.44$ ), methacrylic (2-methylpropenoic) acid CH<sub>2</sub>=C(Me)COOH ( $pK_a = 4.66$ ), and crotonic (*trans*-2-butenoic) acid *trans*-MeCH=CHCOOH ( $pK_a = 4.69$ ).

Complex	Raman, $cm^{-1}$	IR, $cm^{-1}$						
	v(C=C)	v(C=C)	$v_{as}(CO_2)$	$v_s(CO_2)$	Δν			
$Pd_{3}(\mu-CH_{2}=C(Me)CO_{2})_{6}(3)$	1652	1652	1574	1407	167			
$Pd_3(\mu-MeCH=CHCO_2)_6(4)$	1653	1652	1568	1406	162			
$Pd_3(\mu-PhCH=CHCO_2)_6(5)$	1635	1632	1570	1389	181			
$Pd_{3}(\mu-(Me)CH=CH(Me)CO_{2})_{6}$ (6) [15]	—	1656	1582	1414	168			

**Table 3.** Spectral data for  $\alpha$ -unsaturated palladium carboxylates 3–6

Only one complex with an unsaturated carboxylic acid—palladium tiglate  $Pd_3(\mu$ -MeCH=C(Me)CO<sub>2</sub>)<sub>6</sub> has been structurally characterized [15]. The complex contains a trinuclear metallacycle on the sides of which the bridging carboxylate groups are located. The Pd–Pd distances in this complex are within 3.093–3.171 Å and do not differ from the Pd–Pd distances in palladium acetate **1**, in which the average Pd–Pd distance is 3.164 Å [1].

Binary  $\alpha$ -unsaturated palladium carboxylates have been synthesized by substitution of acetate groups in **1** with  $\alpha$ -unsaturated acids:

 $Pd_3(\mu-MeCO_2)_6 + RCO_2H \rightarrow Pd_3(\mu-RCO_2)_6 + MeCO_2H$ , where  $R = CH_2=C(Me)$ , MeCH=CH, PhCH=CH, or MeCH=C(Me).

The above palladium  $\alpha$ -carboxylates were synthesized from palladium acetate **1**, produced by our original procedure. This acetate was free from HNO<sub>3</sub> decomposition products and afforded high yields and purity of a target complex, which we failed to achieve using commercial palladium acetate.

It should be noted that different methods, including multistage, time-consuming processes [18], have been used to purify commercial palladium acetate **2**. In the procedure developed by us, the initial compound for synthesis of palladium acetate **1** is  $(NH_4)_2PdCl_4$ ; the ammonia in this complex promotes the intramolecular reduction of palladium and facilitates the washing of the product from the traces of outer-sphere chloride ions.

According to analytical data, the ratio Pd : RCOO = 1 : 2 persists in the resulting carboxylates. The spectroscopic data for complexes 3-5 are summarized in Table 3.

The Raman and IR spectra have shown that the double bond of methacrylic, crotonic, and cinnamic acids is not involved in the bonding of the  $\alpha$ -carboxy-late ion to palladium; i.e., the v(C=C) values for these complexes remain close to the values observed for the initial acids and palladium tiglate [15]. The stretching vibration frequencies  $v_{as}(CO_2)$  and  $v_s(CO_2)$  and the splitting  $\Delta v = 162-181 = \text{cm}^{-1}$  for the synthesized carboxylates, as well as their coincidence with the corresponding frequencies of palladium tiglate [15], are evidence that the carboxylate ligands are bridging, which has been proved by structural data [15]; this fact allows us to conclude that complexes **3–5** have a structure similar

to that of palladium tiglate  $Pd_3(\mu$ -RCO<sub>2</sub>)<sub>6</sub> (6). Thus, complexes 3–5 contain a trinuclear metallacycle on the sides of which the corresponding carboxylate groups are arranged in pairs. Complexes 3–5 are readily soluble and stable in nonpolar solvents. However, attempts to carbonylate them in a benzene solution led to the reduction of the complexes to Pd(0).

It has been reported [19] that the carbamoyl moiety =N-C(=O)- is generated by conversion of secondary amines to carbamoyl chlorides, intermediates in the synthesis of carbamates and urea, through the formation of palladium carbamoyl complexes  $PdCl_{(2-x)}(CONRR')_{x}L_{2}$  (x = 1, 2) in the reaction of  $PdCl_2L_2$  (L<sub>2</sub> is 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen)) with NHRR' (where NRR' is CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>N (piperidine) or CH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)CH<sub>2</sub>N (morpholine)) with carbon oxide. The use of unsaturated palladium carboxylates in analogous processes can open new possibilities for the known reactions, for example, allows one to bypass the stage of formation of complexes with stabilizing diamines, bipyridine and phenanthroline, and to use the already synthesized aminate complexes, in particular, with secondary amines, as initial compounds for carbonylation.

We have synthesized aminate complexes of  $\alpha$ -unsaturated carboxylates with secondary amines *trans*-PdA<sub>2</sub>(RCO<sub>2</sub>)<sub>2</sub> (A is morpholine (M) C<sub>4</sub>H<sub>9</sub>NO, methylmorpholine (MM) C<sub>5</sub>H<sub>11</sub>NO, or thiomorpholine (MS) C<sub>4</sub>H<sub>9</sub>NS). The spectral characteristics of these complexes are presented in Table 4.

Comparison of the  $v_{as}(CO_2)$  and  $v_s(CO_2)$  frequencies of  $\alpha$ -unsaturated palladium carboxylates with morpholine, 4-methylmorpholine, and thiomorpholine (7-14) (Table 4) points to a weak effect of the conjugated double bond on the character of the -COO group monodentately bound to palladium: their vibrational frequencies correlate with analogous frequencies for 14 and the  $(MeCO_2)_2Pd(C_4H_9NO)_2$  complex [20]. According to X-ray crystallographic data, the conjugation of the C(2)=C(3) double bond of the coordinated acid residue with the COO<sup>-</sup> moiety in 10 lacking hydrogen bonds follows from the value of the torsion angle  $O(1)C(1)C(2)C(3) = 173.11^{\circ}$  close to the perfect straight angle (180°). The v(Pd–N) frequency for 7– 13 is the same being 296  $\text{cm}^{-1}$ . It should be noted that the reaction of palladium crotonate 4 with thiomorpholine  $C_4H_0NS$  at the reagent ratio Pd : MS = 1 : 2 gives the

Complex	Raman,	IR, $cm^{-1}$						
Complex	$cm^{-1}v(C=C)$	v(C=C)	$v_{as}(CO_2)$	$v_s(CO_2)$	Δν			
$(CH_2 = C(Me)CO_2)_2 Pd(C_4H_9NO)_2(7)$	1640	1641	1568	1354	214			
$(MeCH=CHCO_2)_2Pd(C_4H_9NO)_2(8)$	1654	1656	1582	1348	234			
$(PhCH=CHCO_2)_2Pd(C_4H_9NO)_2(9)$	1638	1636	1588	1352	236			
$(MeCH=CHCO_2)_2Pd(C_5H_{11}NO)_2(10)$	1659	1656	1600	1336	264			
$(PhCH=CHCO_2)_2Pd(C_5H_{11}NO)_2(11)$	1639	1636	1576	1336	240			
$(CH_2 = C(Me)CO_2)_2 Pd(C_5H_{11}NO)_2$ (12)	1641	1641	1592	1328	264			
$(MeCH=CHCO_2)_2Pd(C_4H_9NS)_2(13)$	1661	1661	1568	1343	225			
$[(MeCH=CHCO_2)Pd(C_4H_9NS)]_2(14)$	1660	1660	1570	1345	225			
$(MeCO_2)_2Pd(C_4H_9NS)_2(15)$	—	—	1591	1378	213			
$(MeCO_2)_2Pd(C_4H_9NO)_2 \cdot H_2O$ [20]	_	_	1575	1338	237			

Table 4. Spectral data for *trans*-aminate complexes of  $\alpha$ -unsaturated carboxylic acids 7–14 and complexes with acetic acid for comparison 15 and [20]

Table 5. Selected bond lengths (Å) in complexes 8, 8a, 10, 12, and 16–18

Complex	Pd-N	Pd–O	C=C	C–O(Pd)	C–O <sub>term</sub>	NH…O
$(MeCH=CHCO_2)_2Pd(C_4H_9NO)_2(8)$	2.054(2)	2.004(1)	1.288(3)	1.283(2)	1.227(2)	2.771(2)
$(MeCH=CHCO_2)_2Pd(C_4H_9NO)_2(8a)$	2.052(2)	2.009(1)	1.293(3)	1.289(2)	1.235(2)	3.023(2)
$(MeCH=CHCO_2)_2Pd(C_5H_{11}NO)_2(10)$	2.122(5)	2.028(5)	1.332(9)	1.313(7)	1.245(8)	_
$(CH_2 = C(Me)CO_2)_2Pd(C_5H_{11}NO)_2$ (12)	2.059(1)	2.010(1)	1.306(3)	1.291(2)	1.234(2)	3.091(2)
$(OC_4H_8NH)_2Pd[OC_4H_8NC(=O)]$						
$MeCH=CHCO_2) \cdot H_2O(16)$	2.077(2) 2.077(2)	2.138(2)	1.316(3)	1.266(3)	1.250(3)	2.813(3) 3.017(3)
$(C_4H_{10}NO)^+(MeCH=CHCO_2)^-(17)$	_	_	1.314(8)	_	1.257(6 1.277(6)	2.707(5) 2.628(5)
$(C_4H_{10}NS)^+(MeCH=CHCO_2)^-(18)$	—	_	1.315(5) - 1.329(5)	—	1.251(4)— 1.275(4)	2.675(4)— 2.694(4)
$(MeCO_2)_2Pd(C_4H_9NO)_2 \cdot H_2O$ [20]	2.047(4)	2.017(3)	_	1.272(5)	1.238(6)	3.038(7)

 $(MeCH=CHCO_2)_2Pd(C_4H_9NS)_2$  complex (13) in which thiomorpholine coordinated through the nitrogen atom rather than through the sulfur atom, like in compounds with morpholine and 4-methylmorpholine (8 and 10, respectively). The reaction at the ratio Pd : MS = 1 : 1 leads to the binuclear complex  $[(MeCH=CHCO_2)Pd(C_4H_9NS)]_2$  (14) with the bridging thiomorpholine molecules coordinated to palladium through both the nitrogen atom (v(Pd-N) at 296 cm<sup>-1</sup>) and the sulfur atom (v(Pd–S) at 344 cm<sup>-1</sup>), with retention of the monodentate coordination of the crotonate ions, but in the *cis* position,  $v_{as}(CO_2) =$ 1570 cm<sup>-1</sup> and  $v_s(CO_2) =$  1345 cm<sup>-1</sup>. The probable structure of complex **14** is shown in Fig. 1. It should be noted that the  $v_{as}(CO_2)$  and  $v_s(CO_2)$  values for monoand binuclear complexes with thiomorpholine **13** and **14** do not change and point to the lack of the effect of the position of the carboxylate groups on their spectral



Fig. 1. Complex  $[(MeCH=CHCO_2)_2Pd(C_4H_9NS)]_2$  (14).



**Fig. 2.** Molecular structure of polymorphs **8**. Thermal ellipsoids are drawn at the 50% probability level. Here and in Figs. 3, 5, and 7, dashed lines show hydrogen bonds. (a) **8** (from  $C_6H_6$ ) and (b) **8a** (from  $CH_2Cl_2$ ).

characteristics. This is likely a result of the complex electron density redistribution in the  $O_2PdNS$  system of complex 14.

Single crystals of palladium complexes **8**, **10**, and **12** have been studied by X-ray crystallography. Figures 2-5 show the structures of these complexes, and Table 5 presents the bond lengths in *trans*-aminate complexes of  $\alpha$ -unsaturated carboxylic acids. Accord-



Fig. 3. Layers in structure 8a.

ing to X-ray crystallographic data, all aminate complexes of palladium  $\alpha$ -carboxylates with morpholine derivatives-8, 8a, 10, and 12-are centrosymmetric monomers in which the palladium atom has a typical square-planar environment composed of the nitrogen atoms of two coordinated molecules of morpholine (or its derivatives) and two oxygen atoms of the transarranged terminal crotonate groups. Noteworthy is the elongation of the Pd-N bond in complex 10 with methylmorpholine to 2.122(5) Å as compared with complex 8 with morpholine (2.054(2) Å), which is evidence of steric hindrances caused by coordination of 4-methylmorpholine to palladium, which can be explained by the existence of the methyl substituent at the nitrogen atom located in the equatorial position, whereas the N(1)-Pd(1) bond in in axial orientation to the morpholine ring with a chair conformation.

In crystal structure of 8, only intramolecular hydrogen bonds NH···O are observed (Fig. 2), while in its polymorph 8a and compound 12, all hydrogen bonds are intermolecular and combine neighboring complexes into layers (Figs. 2, 3, and 5; Table 5).

It has turned out that the carbonylation of the synthesized aminate  $\alpha$ -unsaturated palladium carboxylate complexes is accompanied by their reduction to Pd(0). Therefore, we have used a new approach to the synthesis of palladium carbamoyl carboxylates through the amination of reaction of palladium carbonyl crotonate with a secondary amine, morpholine. The reaction of palladium carbonyl crotonate Pd<sub>4</sub>( $\mu$ -CO)<sub>4</sub>( $\mu$ -MeCH=CHCO<sub>2</sub>) with morpholine was accomplished in toluene at room temperature. Palladium carbonyl crotonate was synthesized through the substitution of the acetate ion in palladium carbonyl



Fig. 4. Molecular structure of complexes (a) 10 and (b) 12. Thermal ellipsoids are drawn at the 50% probability level.



Fig. 5. Layers in structure 12.

carboxylate with appropriate acid to give  $Pd_4(\mu-CO)_4(\mu-MeCH=CHCO_2)$  [17].

The reaction scheme is shown in Fig. 6. First, palladium carbonyl crotonate disproportionates to give Pd(0) and a Pd(II) complex. After separation of palladium metal, two types of single crystals were obtained from the mother liquor at 4°C: palladium carbamoyl crotonate *trans*- $(OC_4H_8NH)_2Pd[OC_4H_8NC(=O)](MeCH=$  CHCO<sub>2</sub>) · H<sub>2</sub>O (**16**) and morpholonium crotonate  $(C_4H_{10}NO)^+(MeCH=CHCOO)^-$  (**17**). After separation of these crystals, the addition of methylene chloride to the mother liquor gives the third type of crystal **8a** of the same composition as the *trans*-(MeCH=CHCO<sub>2</sub>)<sub>2</sub>Pd(C<sub>4</sub>H<sub>8</sub>NO)<sub>2</sub> complex (**8**). However, X-ray crystallography has shown that the reaction leads to isomer **8a** of complex **8**.

$$Pd_{4}(\mu-CO)_{4}(\mu-MeCH=CHCO_{2})_{4} \xrightarrow{C_{4}H_{8}ONH} \overbrace{C_{6}H_{5}Me}^{Pd(0)} Fd_{6}(C_{4}H_{8}NH)_{2}Pd[OC_{4}H_{8}NC(=O)](MeCH=CHCO_{2}) \cdot H_{2}O (16) (C_{4}H_{10}NO)_{2}^{+}(MeCH=CHCO_{2})^{-} (17) (C_{4}H_{10}NO)_{2}^{+}(MeCH=CHCO_{2})^{-} (17) Pd(MeCH=CHCO_{2})_{2}(C_{4}H_{9}NO)_{2} (8a) (point group Pccn)$$

Fig. 6. Scheme of transformations of palladium carbonyl crotonate in the reaction with morpholine.

The spectral characteristics of reaction products **16**, **8a**, and **17** are summarized in Table 6. The v(C=C),  $v_{as}(CO_2)$ , and  $v_s(CO_2)$  frequencies for all these compounds are nearly identical. The vibrational frequencies of the coordinated morpholine molecules in **8a** and **16** also do not differ from the v(NH) values for other complexes (Table 4) with *trans*-arranged amines coordinated to palladium through the nitrogen atoms.

In complex **16** (Fig. 7), the palladium atom has a square-planar environment with *trans*-arranged atoms N-Pd-N and O-Pd-C. The palladium atom is bonded to two *trans*-arranged morpholine molecules with a somewhat elongated Pd-N distance (2.077(2) Å) as compared with the Pd-N distance in complex **8a** (2.052(2) Å).

The Pd–C distances are somewhat shortened (1.958(2) Å) as compared with the Pd–C distances in the initial palladium carbonyl crotonate (1.980(2)-1.986(2) Å [17]).

The Pd–O distances to the monodentately coordinated carboxylate group are 2.138(2) Å in complex **16** and 2.009(1) Å in aminate complex **8a**. The elongation of the Pd–O bond by 0.13 Å can be a result of the effect of the *trans* carbamoyl ligand, as well as of an intricate system of rather short hydrogen bonds involving solvate water molecules, which form heir chains along the *ac* diagonal (Fig. 8).

The second product of the reaction of morpholine and palladium carbonyl crotonate is morpholonium crotonate  $(C_4H_{10}NO)^+(MeCH=CHCOO)^-$  (17). Formation of the morpholonium cation  $C_6H_8ONH_2^+$ as a result of hydrogen bonding with the carbonyl oxy-



**Fig. 7.** Molecular structure of complex **16**. Thermal ellipsoids are drawn at the 50% probability level.

gen atoms of the crotonate anion is accompanied by a low-frequency shift of the  $-NH_2^+$  stretching vibration band of morpholonium crotonate, which is observed

Compound		IR, cm <sup>-1</sup>							
Compound	v(C=C)	v(C=C)	$v_{as}(CO_2)$	$v_s(CO_2)$	v(NH)	v(CO) carbamoyl	ν(H <sub>2</sub> O)		
$(C_4H_9NO)_2Pd(MeCH=CHCO_2)_2(8a)$	1654	1656	1580	1348	3182	_	_		
$\begin{array}{l} (OC_4H_8NH)_2Pd[OC_4H_8NC(=O)](MeCH=CHCO_2) \\ H_2O \ \textbf{(16)} \end{array}$	1659	1656	1513	1345	3171	1576	3402		
$(C_4H_{10}NO)^+(MeCH=CHCO_2)^-$ (17)	-	1656	1516	1375	_	—	_		

Table 6. Spectral characteristics  $(cm^{-1})$  of compounds 8a, 16, and 17



Fig. 8. Hydrogen-bonded chains in structure 16.

as a moderate broad band with several submaxima in the range  $2000-2600 \text{ cm}^{-1}$ . Selected bond lengths in complexes **8a**, **16**, **17**, and **18** are presented in Table 5.

It should be noted that, when thiomorpholine was added to a solution of palladium carbonyl crotonate, only thiomorpholonium crotonate  $(C_4H_{10}NS)^+(MeCH=CHCOO)^-$  (18) was isolated.

X-ray crystallographic data for compounds **17** and **18** demonstrate that the morpholinium and thiomorpholinium cations in crystals are linked with crotonate anions through strong, almost linear hydrogen bonds NH…O to form chains (Fig. 9, Table 4).

The third product of amination of palladium carbamoyl crotonate is the *trans*- $(C_4H_9NO)_2Pd(MeCH=$  $CHCO_2$ )<sub>2</sub> complex (8a) of the same composition as complex 8 but differing from it according to singlecrystal and powder diffraction data: a crystal of complex 8 obtained from benzene (Fig. 2a) belongs to point group  $P2_1/n$ , whereas a crystal of complex 8a obtained from CH<sub>2</sub>Cl<sub>2</sub> belongs to point group Pccn (Fig. 2b). This difference is due to formation of different types of hydrogen bonds: only intramolecular hydrogen bonds NH---O are formed in the crystal structure of 8, whereas exclusively intermolecular hydrogen bonds are formed in the structure of complex 8a; i.e., the type of hydrogen bond network and, hence, the type of crystal lattice is determined in this case by the nature of the solvent.



Fig. 9. Hydrogen-bonded chains in structures (a) 17 and (b) 18.

Thus, when studying the interaction of a secondary amine-morpholine-with palladium carbonyl crotonate, we discovered a new reaction of formation of the carbamoyl moiety =N-C(=O)- as a result of inner-sphere transformations of the coordinated carbonyl in palladium carbonyl crotonate under the action of morpholine, which lead to palladium cartrans-(OC<sub>4</sub>H<sub>8</sub>NH)<sub>2</sub>Pd bamovl crotonate. The  $[OC_4H_8NC(=O)](MeCH=CHCO_2) \cdot H_2O \text{ complex} (16)$ is the first transition-metal carbamovl carboxylate complex where the anion is an  $\alpha$ -unsaturated carboxvlate ion. Knowledge of the structure and properties of complex 16 can contribute to the understanding of the mechanisms of carbonylation reactions catalyzed by palladium carboxylates [21].

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