Synthesis and spectral studies of 1,3-diketonate derivatives of *ortho*-palladated α-arylalkylamines

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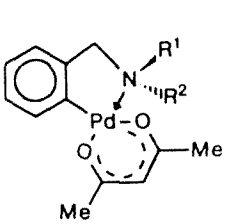
Synthesis of acetylacetonate derivatives of a series of *ortho*-palladated complexes based on secondary and tertiary α-arylalkylamines was described. Their structures and stereochemistry were elucidated by IR, UV, ^{1}H NMR, and CD spectra. Fragmentation processes of these complexes and some model compounds were studied by mass spectrometry (EI). An unusual rearrangement of a molecular ion involving migration of the hydrogen atom from the alkylaminoalkyl group to the palladium atom to form a hydride intermediate followed by the elimination of PdH was observed. The rearrangement occurs through isomerization of the η^2-*O,O'*-coordinated β-diketonate ligand to the η^1-C-bonded diketonyl form to give the coordinationally unsaturated metal center.

Key words: cyclopalladated complexes, mass spectrometry, circular dichroism spectra.

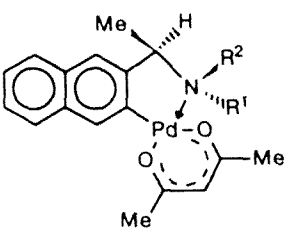
Intense development of the chemistry of cyclopalladated compounds[1,2] is caused by the easy direct intramolecular activation of aromatic and aliphatic C—H bonds, which provides a possibility of subsequent using the Pd—C bonds formed for highly regioselective functionalization of organic compounds of various classes.[3,4] NMR spectroscopy is widely used in structural studies of cyclometallated compounds[5,6]; however, the mass spectra of these compounds, which are of significance in both theoretical and practical respects, are almost unstudied. Mass spectrometry of transition metal complexes is important as both a method for obtaining certain structural information and a unique method for studying the reactivity of organic ligands specifically fixed on a metallic matrix[7] under conditions without solvation effects.

The purpose of this work is the synthesis of a series of acetylacetonate derivatives of *ortho*-palladated complexes based on secondary and tertiary α-arylalkylamines (**1—3**) and study of their structures by IR, ^{1}H NMR, UV, and CD spectroscopies and mass spectrometry.

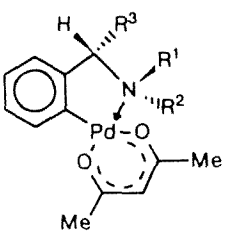
Mononuclear complexes **1—3** were prepared in 68—97 % yields by the reactions of the corresponding dimeric complexes **4** [8—10] with small excess acetylacetone and potassium hydroxide in methanol at room temperature. This method for synthesis of acetylacetonate derivatives of cyclopalladated complexes (CPC) is more simple and efficient than the common method for their preparation *via* thallium(I) β-diketonates[11] and does not require chromatographic purification of the products formed.



1a—b



3a—c

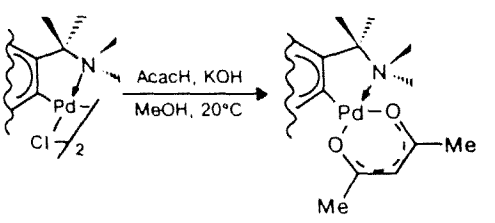


2a—d

1a: R^1 = Pr^i, R^2 = Me;
1b: R^1 = Bu^t, R^2 = H;

2a: R^1 = R^2 = R^3 = Me;
2b: R^1 = Pr^i, R^2 = R^3 =Me;
2c: R^1 = Pr^i, R^2 = H, R^3 = Me;
2d: R^1 = Me, R^2R^3 = $(CH_2)_3$;

3a: R^1 = R^2 = Me;
3b: R^1 = Pr^i, R^2 = Me,
3c: R^1 = Pr^i, R^2 = H



4 **1—3**

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Table 1. Constants, yields, and data of elemental analysis for complexes **1—3**

Compound	Yield (%)	M.p. °C	$[\alpha]_D^{21}$ deg.*	Found / Calculated (%) C	H	N	Pd	Empirical formula
1a	68	92.5—93	—	52.54 52.25	6.06 6.30	3.76 3.81	28.92 28.93	$C_{16}H_{23}NO_2Pd$
2a	91	130—131	16.7	50.92 50.93	5.68 5.98	3.98 3.96	30.06 30.08	$C_{15}H_{21}NO_2Pd$
2b	97	167—168	106	53.26 53.48	7.07 6.60	3.65 3.67	27.53 27.87	$C_{17}H_{25}NO_2Pd$
2c	95	85—87	5.6	51.76 52.25	6.30 6.30	3.91 3.81	28.17 28.93	$C_{16}H_{23}NO_2Pd$
3a	79	159—160	55.6	56.17 56.52	5.68 5.74	3.50 3.47	26.42 26.35	$C_{19}H_{23}NO_2Pd$
3b	91	125—126	−143	58.77 58.41	6.35 6.30	3.32 3.24	24.32 24.64	$C_{21}H_{27}NO_2Pd$
3c	71	100—101	−50.0	57.71 57.49	6.20 6.03	3.36 3.35	26.02 25.47	$C_{20}H_{25}NO_2Pd$

* Specific rotation was measured in chloroform at a concentration of 0.36 g/100 mL.

Table 2. Parameters of ^1H NMR spectra of compounds **1a**, **2a—c**, and **3a—c** in $CDCl_3$ (δ, ppm, *J*/Hz)

Compound	CH_3CO (s, 3 H)	$CHAc_2$ (s, 1 H)	$CH(CH_3)_2$ (d, 3 H, J = 6.5)	$CH(CH_3)_2$ (м, 1 H)	NCH_3 (s, 3 H) or NH (br.s, 1 H)	$CHCH_3$ (d, 3 H, J = 6.5)	$CHCH_3$ (к, 1 H, J = 6.5)	Aromatic protons (м)
1a	1.84; 1.94	5.23	1.20; 1.48	3.30	2.89	*	*	6.82—7.47 (4 H)
2a	1.88; 1.98	5.30	—	—	2.57; 2.85	1.48	3.92	6.80—7.48 (4 H)
2b**	1.93; 2.02	5.29	1.11; 1.75	3.40	2.50	1.77	3.94	6.85—7.25 (4 H)
2c**	1.85; 1.96	5.24	1.26; 1.32	3.08	3.36***	1.62	3.96	6.68—7.26 (4 H)
3a	1.88; 2.02	5.32	—	—	2.57; 2.87	1.53	4.03	7.18—7.90 (6 H)
3b**	1.88; 2.03	5.26	1.00; 1.66	3.19	2.45	1.80	3.96	7.15—7.76 (6 H)
3c**	1.88; 2.06	5.30	1.31; 1.24	3.07	3.37***	1.73	4.10	7.16—7.78 (6 H)

* 3.55, 4.17 (d, J = 14.5, AB-system, CH_2).

** Assignment of the signals of protons of Me groups of *N*-isopropyl and α-methylbenzyl substituents was confirmed by double homonuclear resonance.

*** The position of the signal of the proton of the NH group substantially depends on the concentration of the solution.

The composition and structure of complexes **1—3** are confirmed by the data of elemental analysis (Table 1), ^1H NMR (Table 2), UV, and CD spectroscopies (Table 3), and by comparison of their spectral parameters to those for complex **2b**, whose structure was established previously by the X-ray diffraction method.[12]

The IR spectra of all complexes contain three bands (or two bands and a shoulder) at 1585 to 1595, 1548 to 1580, and 1520 to 1525 cm^{-1} (Table 3), which can be assigned by analogy with the IR spectrum of bis(acetylacetonato-*O,O*)palladium(II) (**5**)[13] to symmetric stretching vibrations of the C=O bonds, out-of-plane vibrations of the C—H bonds, and asymmetric stretching vibrations of the C=C=C bonds, respectively (Table 3). As compared to symmetric complex **5**, compounds **1—3** are characterized by a substantial (by 17 to 27 cm^{-1}) high-frequency shift of the band of the symmetric stretching vibrations of the C=O bond, which is likely related to the great *trans*-effect of the σ-bonded carbon center that weakens one of the two Pd—O bonds. The results of the X-ray diffraction study of complex **2b** confirm this assumption: of two Pd—O bonds 2.01 and 2.12 Å in length, this is precisely the bond *trans*-arranged relative to the Pd—C σ-bond that is lengthened; the bond length of the corresponding C=O bond is 1.23 Å, which is by 0.09 Å shorter than the C=O bond *trans*-arranged relative to the donor nitrogen atom (1.32 Å).[12]

Nonsymmetric surrounding of the chelated acetylacetonate ligand manifests itself in the presence of two signals of CH_3CO groups in the ^1H NMR spectra of all complexes (Table 2). The position of these signals agrees with that of the previously studied acetylacetonate de-

Table 3. Parameters of electronic absorption, circular dichroism, and IR spectra of complexes **1—3**

Compound	Electronic spectra		Circular dichroism spectra		IR spectra (ν/cm^{-1})	
	λ_{max}/nm	logε	λ_{max}/nm	[θ]	$\nu_{CC,CO,CH}$	ν_{NH}
1a	228.5, 272.5, 279.5, 312	4.490, 3.624, 3.624, 3.710,	—	—	1522 s, 1561 m, 1592 s	—
2a	225.5, 271, 278, 312	4.502, 3.646 3.638, 3.734	215, 233.5, 273, 315, 450	−19650, +22460, −1755, +2670, −2.4	1523 s, 1580 s, 1595 s	—
2b	226.5, 271, 278, 310	4.495, 3.631, 3.631, 3.709	210, 230, 250, 274, 281.5, 290 sh, 325, 410	+41980, +35420, +23620,−10370, −11280, −5310, +9050, −87.8	1523 s, 1548 m, sh, 1593	—
2c	205, 224 sh 272.5, 278.5, 312	4.776, 4.480, 3.675, 3.681, 3.740	203, 230, 252, 275 sh, 281, 295, 325, 420	+66480, +21760, +10270, −9970, −12240, −12690, +5500, −21.2	1525 s, 1560 s, sh, 1585 s	3210, 3410 br
3a	237, 270 sh, 279, 294 sh, 312.5, 324 sh	4.898, 4.099, 4.085, 3.935, 3.852, 3.750	236, 250, 270 sh, 305, 317, 322.5, 330, 390, 450	−15980, +12350, +2910, −2320, −2470, −2030, −4210 −58.1, +25.7	1520 s, 1555 m, 1588 s	—
3b	238.5, 270 sh, 278, 290 sh, 312.5, 324 sh	4.937, 4.096, 4.080, 3.987, 3.855, 3.774	225, 245, 250, 256, 275 sh, 283, 290 sh, 307, 323, 332.5, 425	−83490, +24470, +10080, −7200, +20510, +25550, −20870, −13680, −19430, −30590, +31.0	1522 s, 1553 m, sh 1588 s	—
3c	237, 270 sh, 278.5, 294 sh, 313, 320 sh	4.881, 4.075, 4.067, 3.952, 3.861, 3.757	223, 245, 257, 270 sh, 291, 333	−71600, +50230, −5343, +9350, +30990, −25380	1525 s, 1572 s, 1589 s	3200 3400 br

rivatives of other cyclopalladated complexes (δ_{Me} 2.03 to 2.15 and 1.82 to 2.13 ppm, $\Delta\delta$ 0.01 to 0.29 ppm)[5] and bis(acetylacetonato-*O,O'*)palladium(II) (δ_{Me} 2.07 ppm, δ_{CH} 5.43 ppm).[14]

The low-field shifts of the signals of protons of the NCH_3 ($\Delta\delta$ 0.42 to 0.91 ppm) or NH groups ($\Delta\delta$ 2.52 ppm) in the spectra of complexes **1—3** compared to those of free ligands confirm that the N→Pd coordination bond is retained in the acetylacetonate derivatives studied.

The characteristic feature of *ortho*-palladated complexes based on *N*-isopropyl-α-arylalkylamines is the existence of the agostic interactions of one of the Me groups of the *N*-isopropyl fragment with the metal atom,[9,10,12,15,16] which is the most pronounced in the case of complexes based on tertiary amines and is distinctly pronounced in an increase in the nonequivalence of two Me groups of the *N*-isopropyl substituent on going from the complexes of secondary amines **2c** and **3c** ($\Delta\delta$ 0.06 to 0.07 ppm) to the derivatives of tertiary amines **2b** and **3b** ($\Delta\delta$ 0.64 to 0.66 ppm). In the case of complex **1a**, which is nonsubstituted at the α-position of the benzyl group, the distance between two doublets has an intermediate value ($\Delta\delta$ 0.28 ppm). One of the possible reasons for these differences can be an increase in folding of the metallacycle after successive introduction of methyl groups to the N atom and then in the α-position of the benzyl group of the ligand. Comparison of the geometric parameters of the metallacycles in the complexes based on secondary[16] and tertiary[12] amines obtained by the X-ray diffraction study confirms this assumption. Another reason for weakening of the agostic interactions (especially in the case of complex **1a** based on the α-nonsubstituted ligand) could be a change in the population of the conformer of the palladacycle with axial orientation of the *N*-isopropyl substituent.

The presence of only one set of signals in the ^1H NMR spectra of complexes **2b,c** and **3b,c** unambiguously proves that they exist as one of the two possible diastereomers, which differ in absolute configuration of the asymmetric donor nitrogen atom. To estimate the configuration of the N*-stereocenter, the complexes were characterized by the CD and UV spectra recorded in methanol (Table 3). Unfortunately, no correct interpretation of these spectra is possible without additional data. Such complexes as **1—3** are the complex chromophoric systems with the heterogeneous donating {$PdCNO_2$} set and contain ligands of two types, each of which is characterized by intrinsic intraligand transitions. Analysis of the literature data on the UV spectra

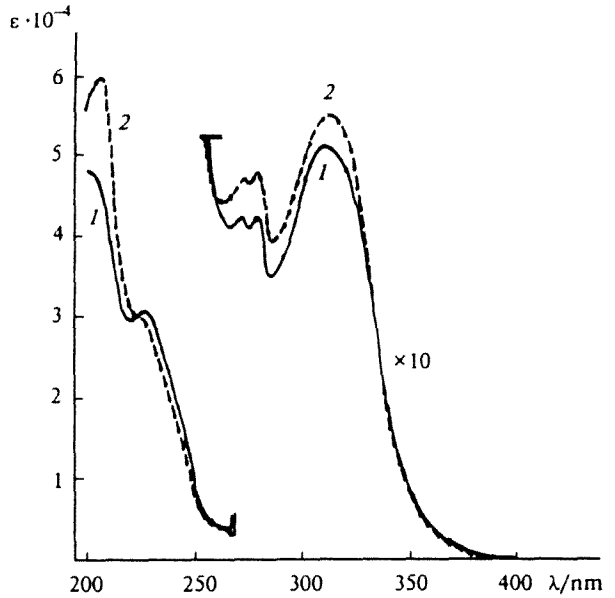


Fig. 1. Electronic absorption spectra of solutions of complexes **2b** (*1*) and **2c** (*2*) in methanol; the long-wave region of the spectra is presented in a tenfold magnification.

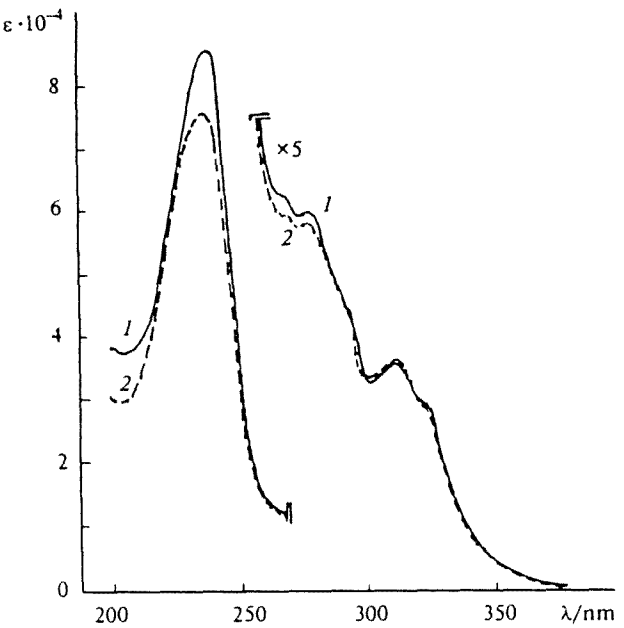


Fig. 2. Electronic absorption spectra of solutions of complexes **3b** (*1*) and **3c** (*2*) in methanol; the long-wave region of the spectra is presented in a fivefold magnification.

of metal bis(β-diketonates)[17,18] and the bis-chelate type cyclopalladated complexes[19] allows one to assume a possibility that several charge-transfer transitions along with d—d-transitions exist in a narrow spectral range.

At the same time, the UV spectra of complexes **1**—**3** in methanol (Table 3, Figs. 1 and 2) are rather simple and contain one or two bands in the short-wave range

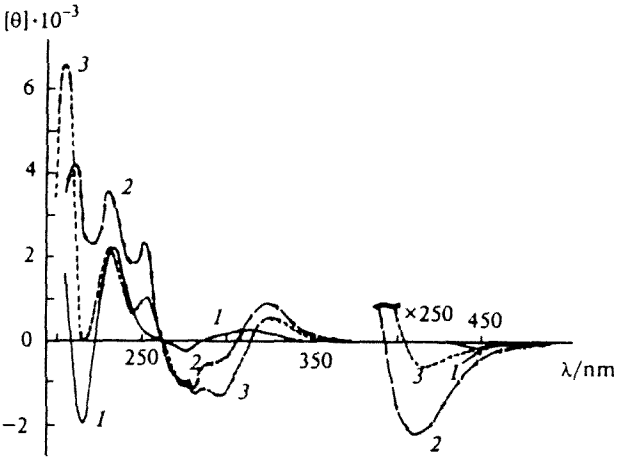


Fig. 3. Circular dichroism spectra of solutions of complexes **2a** (*1*), **2b** (*2*), and **2c** (*3*) in methanol; the long-wave region of the spectra is presented in a 250-fold magnification.

(200 to 240 nm), a band (sometimes with a shoulder) in the long-wave region (310 to 325 nm), and a band or a shoulder with the vibrational structure in the region between them.

The CD spectra of complexes **2a**—**c** and **3a**—**c** are considerably more complicated than the electronic spectra and testify to nonhomogeneity of the bands observed in the electronic spectra (Table 3, Figs. 3 and 4). Comparison of them with chiroptical properties of the known dimeric and mononuclear CPC based on chiral α-arylalkylamines[9,10,15,20] allows one to assume that only the extremum in the range of 325 to 335 nm contains the contribution of one of the spin-allowed d—d-transitions, while the next dichroic maximum at 290 to 300 nm can be assigned to the π—π*-transition of the acetylacetonate ligand, which manifests itself in the UV spectra of sodium acetylacetonate at 288 nm.[21] In all cases, the CD spectra of the complexes based on α-arylalkylamines nonsymmetrically substituted at the N atom (**2b,c** and **3b,c**) are considerably more intense than those of the *N,N*-dimethyl analogs (**2a** and **3a**), which agrees with the appearance of an additional contribution to the optical activity from the asymmetric N atom in the first group of the complexes. The sign of this contribution for the long-wave band corresponding to the spin-allowed d—d-transition is positive for the complexes based on *N*-substituted (*S*)-α-methylbenzylamines (**2b,c**) and negative for the derivatives of (*R*)-α-(2-naphthyl)ethylamine (**3b,c**). The absolute configuration of complex **2b** established previously[12] (S_CR_N) and the close structural similarity of complexes **2** and **3** allow one, taking into account their chiroptical properties, to conclude that complexes **2c** and **3b,c** have absolute configurations of (S_CR_N) and (R_CS_N), respectively.

The CD spectra of complexes **2a**—**c** contain the dichroic band of very low intensity ([θ] from −2.4 to

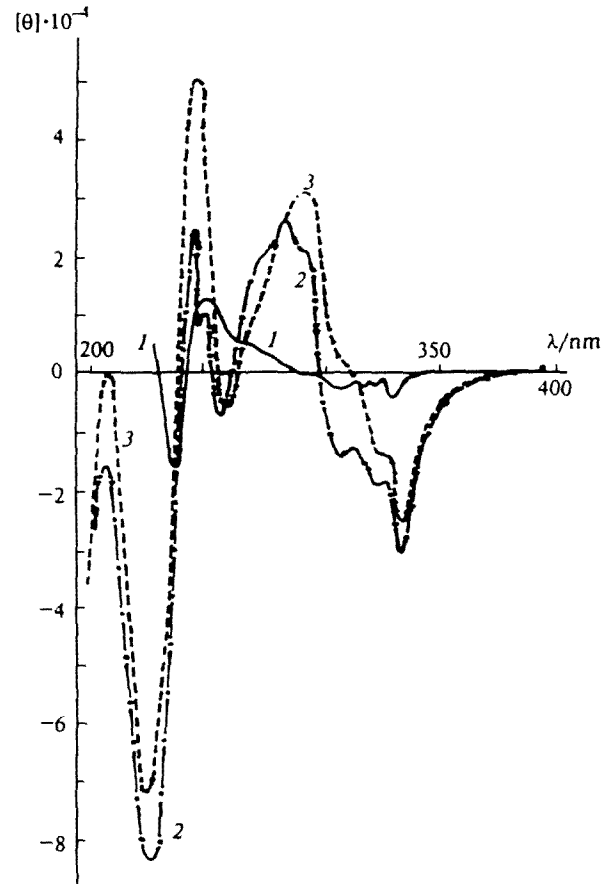


Fig. 4. Circular dichroism spectra of solutions of complexes **3a** (*1*), **3b** (*2*), and **3c** (*3*) in methanol.

−88) in the long-wave range (410 to 450 nm), which can be presumably assigned to one of the triplet spin-forbidden d—d-transitions. The optical activity of this type transitions was observed previously in the CD spectra of both dimeric *ortho*-palladated complexes[20] and simple coordination compounds of α-arylalkylamines such as *trans*-$[Pd(HL)_2Cl_2]$.[22] It is noteworthy that this transition is also sensitive to the asymmetry of the donor N atom; its elliptic character increases by an order of magnitude and more on going from (S_C)-**2a** to ($S_C R_N$)-**2b,c**, and the asymmetric N atom of the absolute configuration (R_N) giving a negative contribution to the optical activity in this range (Table 3, Fig. 3).

Thus, the spectral parameters of complexes **1**—**3** confirm their existence in a stereochemically individual state: with the asymmetric N atom fixed in one of the two possible absolute configurations.

Mass spectrometry has been little used in structural studies of this class of compounds until recently; only the presence of peaks of a molecular ion and several fragmentary ions is established in the majority of cases. According to our data, there is only one publication,[23] which presents the detailed analysis of the mass-spectral behavior under the conditions of fast atom bombardment (FAB) of mono- and binuclear cyclopalladated complexes and intermediate coordination compounds of the *trans*-$[Pd(HL)_2Cl_2]$ type (HL = 1,4-benzodiazepin-2-ones) formed upon their synthesis.

The mass spectra of all complexes **1**—**3** studied contain intense peaks of the corresponding molecular ion ($[M]^+$, Table 4), which testifies to their high stability probably caused by the efficient delocalization of the positive charge in the metallacycles.

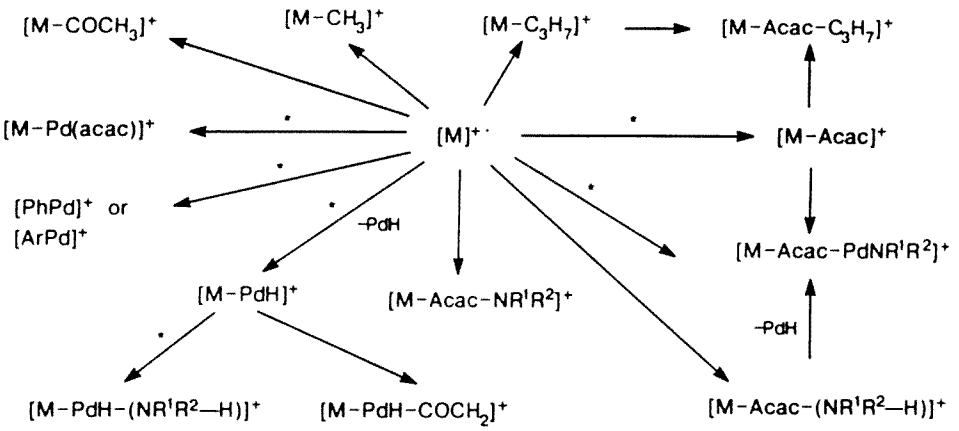
Fragmentation of molecular ions of complexes **1**—**3** occurs *via* several directions presented in Scheme 1. The most general of them are the processes of metal—ligand bond cleavage followed by the ejection of the β-diketonate ligand (free or coordinated with the metal atom) and formation of the $[M-Acac]^+$ or

Table 4. Relative intensities of peaks of main ions (in % of the total ion current) in mass spectra of complexes **1**—**3**

Ion	**1a**	**1b**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**	**3c**
$[M]^+$	16.8	9.6	23.8	32.1	14.5	22.5	26.0	20.9	38.0
$[M-CH_3]^+$	—	0.1	0.3	0.3	0.3	0.1	—	—	—
$[M-COCH_3]^+$	2.3	2.2	2.6	0.7	1.7	0.3	3.3	0.4	3.5
$[M-C_3H_7]^+$	—	—	—	—	1.3	—	—	—	1.3
$[M-Acac]^+$	9.6	20.1	15.1	14.9	18.2	27.7	8.7	8.8	20.2
$[M-PdH]^+$	8.6	2.0	4.3	3.5	3.1	4.2	4.7	3.9	2.7
$[M-Acac-(NR^1R^2-H)]^+$	18.4	—	21.1	17.2	13.3	—	13.9	17.1	7.9
$[M-PdH-C_2H_2O]^+$	—	—	0.7	—	—	—	1.4	—	—
$[M-PdH-(NR^1R^2-H)]^+$	0.4	—	0.5	0.4	0.9	—	0.8	2.3	1.3
$[C_6H_5Pd]^+$ or $[C_{10}H_7Pd]^+$ [a]	0.7	2.0	9.5	6.0	6.7	1.7			
$[Pd]^+$	2.1	3.6	0.3	2.2	0.9	3.6	0.1	0.4	0.8
$[M-Pd(acac)]^+$	16.1	0.8	10.2	9.8	6.9	25.6	5.9	8.7	4.9
$\Sigma[L]^+$ [b]	21.0	55.0	10.9	12.9	32.2	12.3	24.1	30.8	12.6

[a] For derivatives of α-(2-naphthyl)alkylamines, a cluster of peaks centered at m/z 232—235 is observed.
[b] The total intensity of the peaks of the $[L]^+$ ions corresponding to products of decomposition of organic ligands; for complexes **1b** and **2c**, this sum includes the intensities of the peaks of the $[LH]^+$ ions and their fragments formed due to thermolysis of samples in the mass spectrometer.

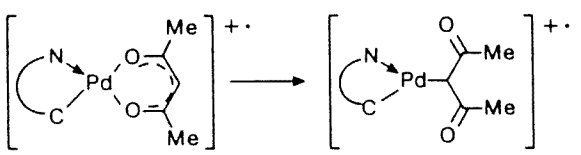
Scheme 1



Note: Ar is naphthyl. Metastable transitions are denoted by asterisks.

$[M-Pd(acac)]^+$ ions, respectively. In the both cases, the aromatic ring remains in the charged fragment, which testifies to a high stability of the ions formed. The yield of the $[M-Acac]^+$ ions increases on going from the complexes based on tertiary amines to the derivatives of secondary amines (for example, from **2b** to **2c** or from **3b** to **3c**), which agrees with a stronger coordination of the secondary amine donor center with the metal atom. Elimination of the β-diketonate ligand from the molecular ion is typical for bis- and tris-chelates of transition metals with β-diketonates[24] and was mentioned, in particular, for hexafluoroacetylacetonate derivatives of some CPC.[25]

Fragmentation of the coordinated acetylacetonate ligand predominantly involves the elimination of the acetyl radical to form $[M-COMe]^+$ ions (see Table 4). This behavior can be explained by the easy rearrangement of the β-diketonate ligand from the *O,O'*-coordinated form ($[M_1]^+$) to the γ-C-bonded state ($[M_2]^+$).

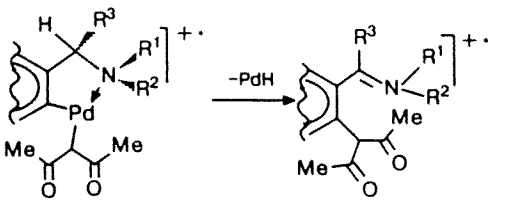


$[M_1]^+$ $[M_2]^+$

Rearrangements of this type are known for palladium(II) and platinum(II) bis(β-diketonate) complexes; they readily occur in solutions, for example, under the action of the appropriate monodentate ligand.[26,27]

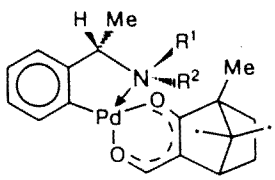
Thus, as in the case of homoleptic β-diketonate complexes,[28] the presence of $[M-COMe]^+$ ions in the mass spectra of acetylacetonate derivatives of *ortho*-palladated compounds can serve as a diagnostic indication of the existence of the molecular $[M_2]^+$ ion.

The $[M_1]^+ \rightarrow [M_2]^+$ isomerization opens the coordination vacancy at the metal atom, which is the main reason for the cross-coupling of two organic ligands in the coordination metal sphere followed by the elimination of neutral palladium(I) hydride.



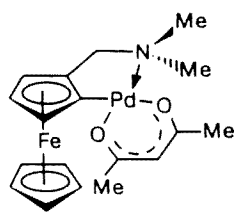
$[M_2]^+$

The formation of the $[M-PdH]^+$ ions from the "open" form of the molecular $[M_2]^+$ ion is testified by a considerable (more than by 7 times) suppression of this process in the case of the complexes (**6a,b**) containing the β-dicarbonyl ligand with the bicyclic framework (see Experimental). In these systems, the rearrangement of the ligand to the γ-C-bonded state should be strongly hindered by steric reasons.



6a: $R^1 = R^2 = Me$

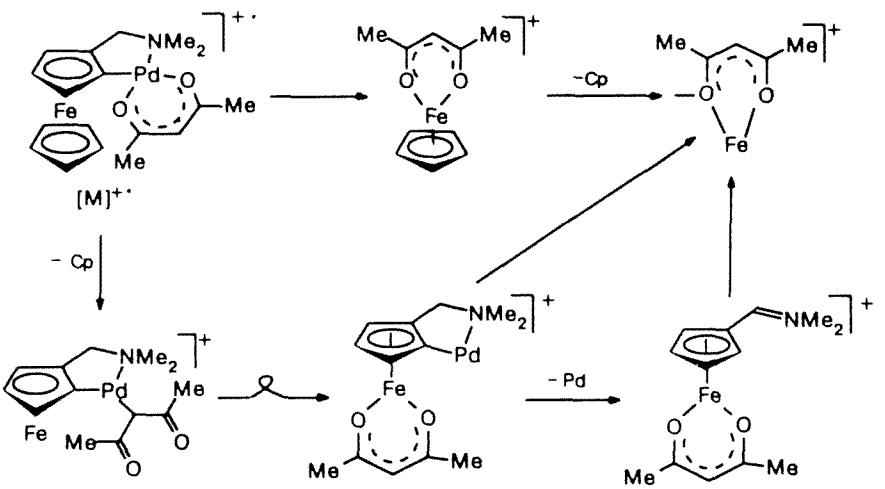
6b: $R^1 = Pr^i$, $R^2 = H$



7

Complexes **6a,b** were obtained in a yield of 89 % as a mixture of diastereomers by the reaction of the corresponding dimeric CPC of type **4** with racemic hydroxymethylenecamphor potassium salt (KL") generated *in situ* by the reaction of HL" with KOH in MeOH.

Scheme 2



The substitution of the phenyl or naphthyl group in complexes **1**—**3** for the ferrocenyl one (complex **7**) also results in the suppression of elimination of PdH. In the molecular ion of this compound, as in other ferrocene derivatives, the charge is predominantly localized on the iron atom,[29] and the main routes of its fragmentation occur *via* migration of the β-diketonate ligand from Pd to Fe to form $[CpFe(acac)]^+$, $[Me_2NCH_2C_5H_4Fe(acac)]^+$, and $[Fe(acac)]^+$ fragments. It is likely that this rearrangement occurs also *via* isomerization of the β-diketonate ligand to the η^1-diketonyl one, which again binds the iron atom according to the diketonate type. The main directions of fragmentation of complex **7** are presented in Scheme 2.

The mass spectra of complexes **1a,b** and **2a**—**d** contain the peak of the ion corresponding to the $[PhPd]^+$ fragment, whose intensity in the most cases is rather high (6 to 10 %). Therefore, observation of the $[ArPd]^+$ fragment can be considered as an useful diagnostic method for confirmation of the *ortho*-palladated structure of this type complexes.

Thus, we found the unusual rearrangement of the molecular ion of the β-diketonate derivatives of *ortho*-palladated α-arylalkylamines initiated by the isomerization of the β-diketonate ligand to the γ-C-bonded form. It involves the migration of the H atom from the alkylaminoalkyl group to the Pd atom followed by the extrusion of palladium(I) hydride and cross-coupling of two aromatic ligands.

Experimental

^1H NMR spectra were recorded on a Tesla BS-497 spectrometer at 100 MHz in $CDCl_3$, using HMDS as an internal standard. CD spectra were recorded in MeOH on a Jasco J-20 spectropolarimeter, and the specific rotation was measured on an automated VNIEKIPRODMASH AI-EPO polarimeter. UV spectra were recorded on a Cary-219 spectrometer in methanol in the range of 200 to 500 nm. IR spectra were recorded on a UR-20 spectrometer in the range of 690 to 3600 cm^{-1} in nujol.

EI mass spectra were recorded on MKh-1320 and Kratos-MS-30 mass spectrometers with a DS-50 system of data collection and processing. The energy of ionizing electrons was 70 eV, the temperature of an ionization chamber was 250 °C, and the temperature of an evaporator of the system of the direct sample injection was 150 to 180 °C. Mass spectra were reduced to the monoisotopic type by the AELITA program[30] on a Nova-2/10 computer.

Mass spectra of all acetylacetonate derivatives contain peaks of $[Hacac]^+$ ions, whose formation is caused by the partial decomposition of the complexes in the mass spectrometer before ionization. This is testified by an increase in the contribution of the peaks of these ions as the temperature of evaporation of the sample increases and by the appearance of the peaks of the $[Dacac]^+$ ions upon simultaneous evaporation of complex **2b** and CD_3OD into the ionization chamber.

Complexes of type **4** were prepared by known procedures[8—10] **[2-(*N*-*tert*-Butylaminomethyl)phenyl-*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (1b)**,[31] **[(S_C,R_N)-2-{1-(*N*-methyl-*N*-isopropylamino)ethyl}phenyl-*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (2b)**,[12] and **(*R*,*S*)-[2-(*N*-methylpyrrolidin-2-yl)phenyl-*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (2d)**[20] complexes were described previously.

(*R*,*S*)-3-(Hydroxymethylene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (HL") was synthesized from racemic camphor by the method described previously[32] in a yield of 22 %, m.p. 75—76 °C.

(*R*,*S*)-[2-(*N*-Methyl-*N*-isopropylaminomethyl)phenyl-*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (1a). Freshly distilled acetylacetone (2.2 mmol) and KOH (2.2 mmol, as a 10 % solution in methanol) were poured into a suspension of (*R*,*S*)-di(μ-chloro)bis-[2-(*N*-methyl-*N*-isopropylaminomethyl)phenyl-*C*,*N*]dipalladium(II) (1 mmol) in 50 mL of anhydrous MeOH. The mixture was stirred for 3 h at ~20 °C, filtered, concentrated *in vacuo* to ~7 mL, and precipitated by slow addition of distilled water. Complex **1a** in a yield of 68 % was obtained after recrystallization from hexane.

The following compounds were synthesized similarly from the corresponding complexes **4**:

[(S_C)-2-{1-(*N*,*N*-Dimethylamino)ethyl}phenyl-*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (2a), **[(S_C,R_N)-2-{1-(*N*-isopropylamino)ethyl}phenyl-2*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (2c)**, **[(R_C)-3-{1-(*N*,*N*-dimethylamino)ethyl}naphth-2-yl-2*C*,*N*](acetylacetonato-*O*,*O*')palladium(II) (3a)**, **[(R_C,S_N)-3-{1-(*N*-methyl-*N*-isopropylamino)ethyl}naphth-2-yl-**

2*C,N*](acetylacetonato-*O,O*')palladium(II) (3b), and **[(R_C,S_N)-3-{1-(*N*-isopropylamino)ethyl}naphth-2-yl-2*C,N*](acetylacetonato-*O,O*')palladium(II) (3c)**.

Constants, yields, and data of elemental analysis for complexes **1a**, **2a—c**, and **3a—c** are presented in Table 1.

[(S_C)-2-{1-(*N,N*-Dimethylamino)ethyl}phenyl-*C,N*]{3-(hydroxymethylene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-onato-*O,O*'}palladium(II) (6a). (*R,S*)-3-(Hydroxymethylene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (0.3750 g, 2.08 mmol) and KOH (0.1168 g, 2.08 mmol, as a 10 % aqueous solution) were successively added to a suspension of (+)$_D$-di-μ-chlorobis[(S_C)-2-{1-(*N,N*-dimethylamino)ethyl}phenyl-*C,N*]dipalladium(II) (0.3016 g, 0.52 mmol) in 75 mL of methanol, and the mixture was refluxed in an argon flow for 7 h. The cooled reaction mixture was filtered and concentrated to 5—7 mL. A colorless finely crystalline complex formed was precipitated by slow addition of water, washed with water, and dried *in vacuo* at ~20 °C. A yield of a mixture of diastereomeric complexes was 0.40 g (89 %), $[\alpha]_D^{20}$ +4.35° (*c* 3.7, chloroform). After triple recrystallization from hot hexane (until the constant specific rotation was achieved), one of the diastereomers (**6a**) was isolated: m.p. 160—162 °C, $[\alpha]_D^{20}$ +50.7° (*c* 2.38, chloroform). Found (%): C, 58.53; H, 6.86; N, 3.05. $C_{21}H_{29}NO_2Pd$. Calculated (%): C, 58.14; H, 6.74; N 3.23. UV spectrum (chloroform), λ_{max}/nm (logε): 332 (3.80); 280 sh (3.62). IR spectrum, ν/cm^{-1}: 1510 s, 1585 w, 1635 s (C=C, C=O, C—H). Mass spectrum (ion, I_{rel}, (%)): $[M]^+$ 2.9; $[M-CO]^+$ 0.8; $[M-PdH]^+$ 0.2; $[M-L"]^+$ 3.9; $[M-L"-CH_2NCH_3]^+$ 3.0; $[L"-O]^+$ 89.2.

[(S_C,R_N)-2-{1-(*N*-Isopropylamino)ethyl}phenyl-*C,N*]{3-(hydroxymethylene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-onato-*O,O*'}palladium(II) (6b) was synthesized similarly from the corresponding dimeric *ortho*-palladated complex (**4**) as a mixture of diastereomers with a yield of 89 %, m.p. 103-105°C, $[\alpha]_D^{20}$ +8.17° (*c* 2.73, chloroform). Found (%): C, 58.50; H, 7.28; N, 3.08; Pd, 23.91. $C_{22}H_{31}NO_2Pd$. Calculated (%): C, 58.93; H, 6.93; N, 3.13. IR spectrum, ν/cm^{-1}: 1510 s, 1635 s (C=C, C=O). UV spectrum (chloroform), λ_{max}, nm (logε): 332 (3.78); 278 (3.63). Mass spectrum (ion, I_{rel} (%)): $[M]^+$ 1.1; $[M-CO]^+$ 0.28; $[M-CO-28]^+$ 0.1; $[M-PdH]^+$ 0.02; $[M-L"H_n]^+$ 51.8 (n = 0 and 1); $[M-L"-NC_3H_7]^+$ 25.9; $[L"-O]^+$ 20.8.

[(*R,S*)-2-{*N,N*-Dimethylaminomethyl}ferrocenyl-*C,N*](acetylacetonato-*O,O*')palladium(II) (7) was synthesized by the known procedure.[51] Mass spectrum (ion, I_{rel} (%)): $[M]^+$ 19.9; $[M-Ac]^+$ 0.3; $[M-Cp]^+$ 0.4; $[M-Cp-Ac]^+$ 1.1; $[M-CpFe]^+$ 7.4; $[M-Acac-NMe_2]^+$ 2.2; $[M-PdCp]^+$ 5.3; $[M-Pdacac]^+$ 14.2; $[M-acacFeCp]^+$ 4.1; $[M]^{2+}$ 0.9; $[CpFeacac]^+$ 3.7; $[CpFeC_6H_6]^+$ 22.6; $[Fe(acac)]^+$ 5.9; $[CpFe]^+$ 7.2; $[Fe]^+$ 0.9; $[Ac]^+$ 3.9.

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References

1. V. V. Dunina, O. A. Zalevskaya, and V. M. Potapov, *Usp. Khim.*, 1988, **57**, 434 [*Russ. Chem. Rev.*, 1988, **57** (Engl. Transl.)].
2. A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
3. A. D. Ryabov, *Usp. Khim.*, 1985, **54**, 253 [*Russ. Chem. Rev.*, 1985, **54** (Engl. Transl.)].
4. M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567.
5. P. J. Steel and G. B. Caugill, *J. Organomet. Chem.*, 1987, **327**, 101.
6. Van der Poel and G. Van Koten, *J. Organomet. Chem.*, 1981, **217**, 129.
7. N. V. Gerbeleu, *Reaktsii na matritsakh* [*Templates Reactions*], Shtiintsa, Kishinev, 1980 (in Russian).
8. V. V. Dunina, O. A. Zalevskaya, and V. M. Potapov, *Zh. Obshch. Khim.*, 1984, **54**, 389 [*J. Gen. Chem. USSR*, 1984, **54** (Engl. Transl.)].
9. O. A. Zalevskaya, V. V. Dunina, V. M. Potapov, L. G. Kuz'mina, and Yu. T. Struchkov, *Zh. Obshch. Khim.*, 1985, **55**, 1332 [*J. Gen. Chem. USSR*, 1985, **55** (Engl. Transl.)].
10. V. V. Dunina, O. A. Zalevskaya, I. P. Smolyakova, and V. M. Potapov, *Zh. Obshch. Khim.*, 1986, **56**, 674 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
11. Y. Fuchita, K. Hiraki, and Y. Kage, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 955.
12. L. G. Kuz'mina, Yu. T. Struchkov, V. V. Dunina, O. A. Zalevskaya, and V. M. Potapov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1807 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1639 (Engl. Transl.)].
13. B. Vickova, B. Strauch, and M. Horak, *Collect. Czech. Chem. Commun.*, 1985, **50**, 306.
14. S. Okeya, Sh.-ichi Ooi, K. Matsumoto, Y. Nakamura, and Sh. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1085.
15. L. G. Kuz'mina, Yu. T. Struchkov, O. A. Zalevskaya, V. V. Dinina, and V. M. Potapov, *Zh. Obshch. Khim.*, 1987, **57**, 2499 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
16. L. G. Kuz'mina, O. Yu. Burtseva, M. A. Porai-Koshits, V. V. Dunina, O. A. Zalevskaya, and V. M. Potapov, *Zh. Obshch. Khim.*, 1989, **59**, 2525 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
17. S. D. Bella, I. Fragala, and G. Granozzi, *Inorg. Chem.*, 1986, **25**, 3997.
18. F. D. Lewis, G. D. Salvi, D. R. Kanis, and M. A. Ratner, *Inorg. Chem.*, 1993, **32**, 1251.
19. R. Schwarz, G. Glieman, Ph. Jolliet, and A. von Zelewsky, *Inorg. Chem.*, 1989, **28**, 742.
20. V. V. Dunina, V. P. Kislyi, N. S. Gulyukina, Yu. K. Grishin, and I. P. Beletskaya, *Metalloorg. Khim.*, 1992, **5**, 1297 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
21. J. P. Fackler, *Prog. Inorg. Chem.*, 1966, **7**, 361.
22. V. V. Dunina, O. A. Zalevskaya, I. P. Smolyakova, V. M. Potapov, L. G. Kuz'mina, Yu. T. Struchkov, and L. N. Reshetova, *Zh. Obshch. Khim.*, 1986, **56**, 1164 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
23. M. A. Cinellu, G. Minghetti, G. Banditelli, A. L. Bandini, B. Pelli, and P. Traldi, *Inorg. Chim. Acta.*, 1989, **161**, 57.
24. J. B. Westmore, in *Mass Spectrometry of Metal Compounds*, Ed. J. Charalambours, Butterworths, London—Boston, 1975, 147.
25. A. R. Siedle, *J. Organomet. Chem.*, 1981, **208**, 115.
26. Sh. Baba, T. Ogura, and Sh. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 665.
27. A. R. Siedle and D. H. Pignolet, *Inorg. Chem.*, 1981, **20**, 1849.
28. B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc. A*, 1968, 1993.
29. J. Charalambours, in *Mass Spectrometry of Metal Compounds*, Ed. J. Charalambours, Butterworths, London—Boston, 1975, 45.
30. Yu. N. Sucharev and Yu. S. Nekrasov, *Org. Mass Spectrom.*, 1976, **11**, 1232.
31. V. V. Dunina, N. S. Gulyukina, I. V. Byakova, and Yu. F. Oprunenko, *Zh. Org. Khim.*, 1994, **30**, 1497 [*J. Org. Chem., USSR*, 1994, **30** (Engl. Transl.)].
32. R. L. Lintvedt and A. M. Fatta, *Inorg. Chem.*, 1968, **7**, 2489.
33. J. C. Gaunt and B. L. Shaw, *J. Organomet. Chem.*, 1975, **102**, 511.

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