Circular dichroism of optically active planar chiral cyclopalladium ferrocene derivatives. Investigation of the dimer—monomer equilibrium

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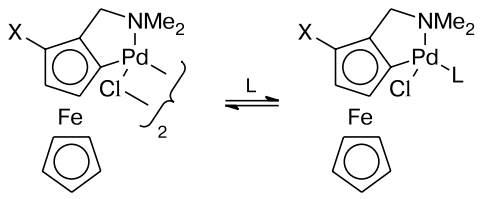
The concentration dependence of the circular dichroism spectra of optically active dinuclear 2-dimethylaminomethylferrocenylpalladium chloride was studied in two solvents. The observed changes in the position and intensity of the Cotton effects were interpreted as a consequence of the dimer—monomer equilibrium.

Key words: chelate palladocycle, ferrocenes, optical activity, circular dichroism, Cotton effects, concentration dependence, dimer—monomer equilibrium.

The cyclopalladation has attracted interest because this reaction is widely used and rather readily proceeds, as well as due to high reactivity, including catalytic activity, of chelate palladocylces and the possibility of their use as liquid-crystalline or chemotherapeutic agents.[1—4] Optically active derivatives of this series are few in number, which is associated with the necessity of separating precursors bearing, as a rule, a chiral center. Planar chiral derivatives of metallocenes derived from achiral substrates by the asymmetric cyclopalladation is a beneficial exception.[5—7] The latter compounds have found wide use in the enantioselective synthesis.[8,9] However, investigations on the circular dichroism[9—15] for palladocycles of the ferrocene series are scarce. To our knowledge, the influence of the concentration on the circular dichroism (CD) spectra has not been studied. Nevertheless, this question is of interests because such metallocycles are generally produced as halide-bridged dimers. Hence, these dimers would be expected to exist in solution in equilibrium with monomers, in which one coordination site at the metal atom is occupied by a solvent molecule.

In the present study, we used the CD method for investigating the behavior of the parent compound, *viz.*, dinuclear 1-chloropalladio-2-dimethylaminomethylferrocene **1**, in two solvents (toluene and ethyl acetate) and the behavior of trisubstituted derivative **2** containing the carboxymethyl group at position 3 in toluene. The CD spectra were found to be dependent on the concentration of the palladocycle (Figs 1 and 2).



1, **2**

X = H (**1**), COOMe (**2**)

The positions of the maxima of two major Cotton effects are consistent with the published data. However, these positions undergo substantial shifts depending on

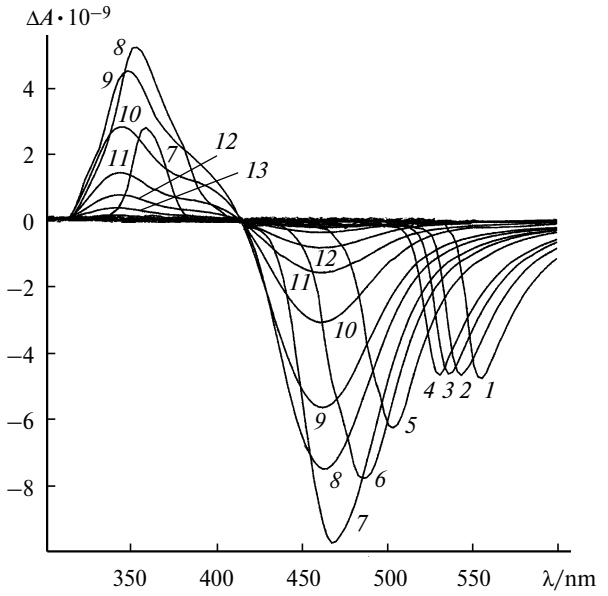


Fig. 1. Circular dichroism spectra of compound **1** in toluene at different concentrations (g L^{-1}): 10.0 (*1*), 7.5 (*2*), 6.0 (*3*), 5.0 (*4*), 3.0 (*5*), 2.0 (*6*), 1.5 (*7*), 1.0 (*8*), 0.75 (*9*), 0.5 (*10*), 0.25 (*11*), 0.125 (*12*), 0.05 (*13*).

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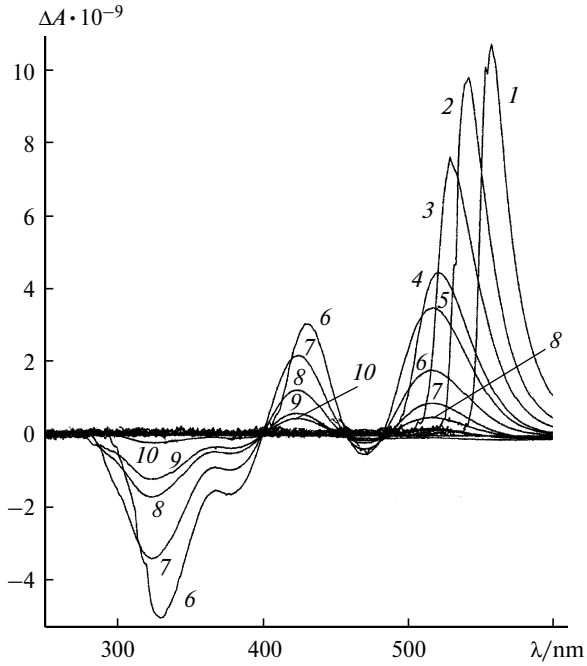

Fig. 2. Circular dichroism spectra of compound **2** in toluene at different concentrations (g L^{-1}): 32.0 (*1*), 16.0 (*2*), 8.0 (*3*), 4.0 (*4*), 2.0 (*5*), 1.0 (*6*), 0.5 (*7*), 0.4 (*8*), 0.2 (*9*), 0.1 (*10*).

the concentration. The experimental data are summarized in Tables 1 and 2 and are presented in Figs 1—3. As Fig. 3 clearly shows, the short-wavelength Cotton effect is observed at high dilution. The long-wavelength Cotton effect is negative for compound **1** in accordance with the S_p configuration and is positive for compound **2**, in which the Pd atom governing the configuration is related to the metal atom in molecule **1** by the mirror symmetry.[8] In this case, the nature of the solvent (toluene or ethyl acetate) has no noticeable effect because the CD spectrum reflects the character of asymmetry of the environment of the chromophore, to be more precise, the replacement of the chiral moiety in the dimer with an achiral solvent molecule. Evidently, the 10-fold change in the concentration has no effect on the isotropic UV spectra and ^{1}H NMR spectra. This was demonstrated by special experiments. The fact that the observed phenomenon is determined by the existence of the dimer—monomer equilibrium is confirmed by the absence of an analogous concentration dependence for the CD spectrum in solutions of an unambiguously mononuclear compound containing the metal atom in the (N^N^C)Pd—C-type tridentate coordination. This compound will be described elsewhere.

Table 1. Circular dichroism (ΔA) and the positions of the maxima of the major Cotton effects in the CD spectrum of compound **1** in toluene depending on the concentration (see Fig. 1)

Spectrum	$-\Delta A \cdot 10^{-6}$	λ_1/nm	$\Delta A \cdot 10^{-6}$	λ_2/nm
1	4642	542	—	—
2	4597	535	—	—
3	4612	529	—	—
4	5124	520	—	—
5	6203	501	—	—
6	7763	486	204	361
7	9659	468	2904	351
8	7504	450	5027	351
9	5629	460	4572	350
10	3049	460	2881	346
11	1540	460	1471	343
12	785	460	811	342
13	313	460	420	342

Experimental

Compound (S_p)-**1**, 83% *ee*, $[\alpha]_D^{20}$ −555° (CH_2Cl_2), was synthesized according to a known procedure[6] in the presence of *N*-acetyl-D-valine as an optical inductor. Compound **2** was synthesized as described earlier.[8]

The CD spectra were measured on a SKD-2 dichrograph (V. A. Engelhard Institute of Molecular Biology and the Institute of Spectroscopy of the Russian Academy of Sciences) in the 250—600 nm range at 23 °C in a 1-cm quartz cell. The instrument was calibrated against D-camphorsulfonic acid.[16] All mea-

Table 2. Circular dichroism (ΔA) and the positions of the maxima of the major Cotton effects in the CD spectrum of compound **2** in toluene depending on the concentration (see Fig. 2)

Spectrum	$\Delta A \cdot 10^{-6}$	λ_1/nm	$\Delta A \cdot 10^{-6}$	λ_2/nm	$-\Delta A \cdot 10^{-6}$	λ_3/nm	$-\Delta A \cdot 10^{-6}$	λ_4/nm
1	10700	555	—	—	—	—	—	—
2	9836	542	—	—	—	—	—	—
3	7609	525	—	—	—	—	—	—
4	4398	520	—	—	—	—	—	—
5	3500	520	448	452	—	—	—	—
6	1812	512	3094	426	—	—	—	—
7	861	510	2154	425	1600	380	5000	330
8	510	510	1200	423	1000	377	3400	325
9	160	510	480	420	350	377	1200	325
10	80	510	125	420	75	377	200	324

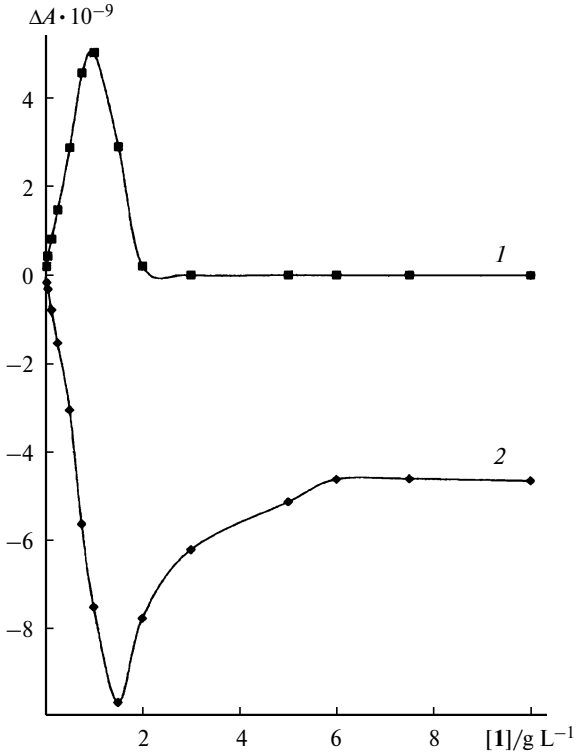

Fig. 3. Circular dichroism (ΔA) for the Cotton effects at 500 (*1*) and 350 nm (*2*) in the CD spectrum of compound **1** in toluene.

surements were carried out with a spectral resolution of 3 nm; the acquisition time was 2.4 s; the scan rate was 35 nm min^{-1}. In all plots and figures, the circular dichroism is expressed in ΔA (difference in absorbance of right- and left-circularly polarized light). Solutions of compound **1** in toluene and ethyl acetate were prepared in the concentration range of 0.05—10.0 and 0.16—5 g L^{-1}, respectively; solutions of compound **2** in toluene, in the concentration range of 0.1—32 g L^{-1}.

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