**6α-Methyl-16α,17α-cyclohexanopregn-4-ene-3,20-dione (3).** A mixture of a solution of product **2** (0.45 g) in 25 mL of EtOH, 5% Pd/C (0.3 g), and 2.5 mL of freshly distilled cyclohexene was boiled with stirring for 28 h. During this period cyclohexane was added three times (3×1.5 mL). The catalyst was filtered off and washed with ethanol. The filtrate was acidified with dilute HCl, and most of the ethanol was removed *in vacuo*. Ice was added to the residue, and the white powder that precipitated was filtered off, washed with water on a filter, and air dried. Chromatographic purification afforded enedione **3** (0.33 g, 73%), m.p. 175—178 °C, which gave no melting point depression with an authentic sample.[9]

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# Bis-*para*-semiquinoid type double cyclopalladation in the series of six-membered two-nitrogen bridged annulene-dihydroannulene ligands

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The cyclometallation reaction known in the series of annulene heteroorganic ligands was extended to six-membered dihydroannulenes with a dinitrogen bridge. Double cyclopalladation of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one azine yielded the first representative of a new class of cross-conjugated diazadipalladatetracycles, *viz.*, 5,10-bis(acetylacetonato)-2,7-dimethyl-2,7-bis(trichloromethyl)-2,7-dihydro-4b,9b-diaza-5,10-dipalladaindeno[2,1-*a*]indene, isolated as a diastereomer mixture of the achiral *meso*-form (*E*-isomer) and a racemate (*Z*-isomer). This reaction offers a method for transition metal-mediated activation of nonreactive C—H bonds at position 2 of cyclohexa-2,5-dienylidene systems and a route toward the very rare chiral polyheteroelement system with rotational symmetry.

**Key words**: azines of α,β-unsaturated carbonyl compounds, 2,5-cyclohexadienones, use of $Pd^{II}$ derivatives in fine organic synthesis, double cyclopalladation, unsaturated metallaheterocycles, organometallic compounds, stereoisomerism, chirality.

The reaction of cyclometallation (also known as *ortho*-metallation) producing π,π-conjugated diazametalladi- and tetracycles (**1**[1], **2**[2]; *cf.* also Ref. 3) was discovered at the end of the 1960s for the benzenoid compound, azobenzene **3**, in which both six-membered rings are aromatic and the N atoms are linked by a π-bond (*cf.* the recently discovered reaction of double cyclometallation of azines of benzaldehyde[4] and benzophenone[5]). In the present work we for the first time extended the annulene type of transformation to a series of six-membered two-nitrogen bridged dihydroannulenes, azines of 4,4-disubstituted 2,5-cyclohexadienones (**4**),

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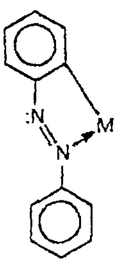
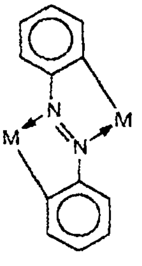
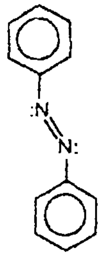
which differ from azobenzene **3** by having a single bond between the two sp$^2$-hybridized N atoms and, therefore, having a semiquinoid (in other words, reduced) character of both six-membered rings (see Refs. 6—8 for other examples of organometallic chemistry of semiquinoid ligands being developed by us).



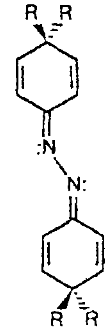
**1**



**2**



**3**

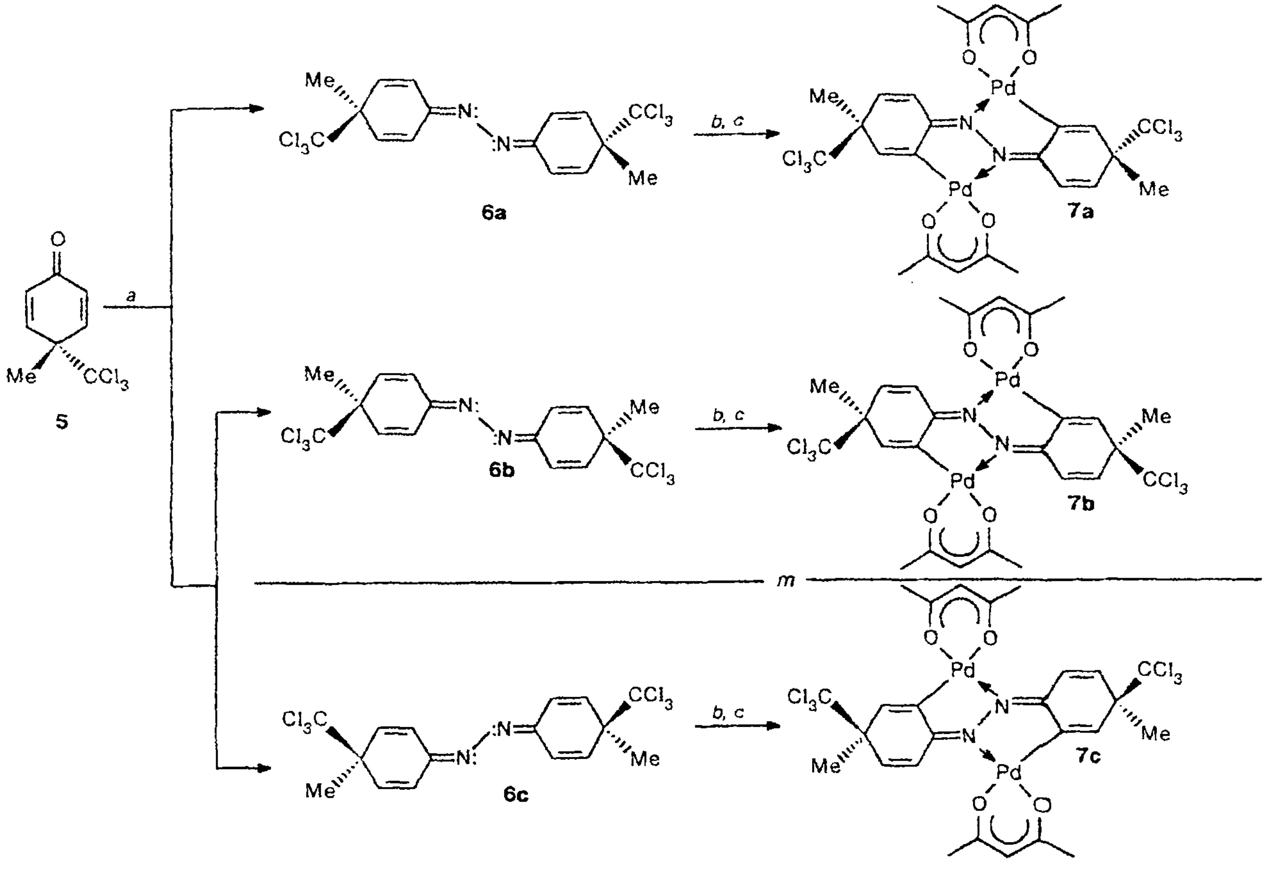


**4**

For realization of this novel strategy we chose 4-methyl-4-trichloromethyl-cyclohexa-2,5-dien-1-one azine (**6**)[9] obtained from dienone **5**. Double cyclopalladation of **5** (Scheme 1) gave the first representative of a new class of cross-conjugated diazadipalladatetracycles, 5,10-bis(acetylacetonato)-2,7-dimethyl-2,7-bis(trichloromethyl)-2,7-dihydro-4b,9b-diaza-5,10-dipalladaindeno[2,1-*a*]indene (**7**), in a yield of ~40%. Its structure was established by elemental analysis and $^1$H NMR spectroscopy.

In the $^1$H NMR spectrum of **7**, the signals of the H$_X$ proton located near the Pd—C bond are shifted considerably upfield of those in the free non-coordinated ligand **6** ($\Delta\delta$ = 0.2). This spectral characteristic indicates the presence of an electron-donor Pd—C bond in the compound synthesized. The clear doubling of the $^1$H NMR resonance signals ($\Delta\nu$ = 2÷10 Hz) in the spectrum of the product **7** indicates that it exists as a mixture of diastereoisomers (in approximately equal amounts, depending on the conditions of isolation) of the achiral *meso*-form (*E*-isomer) **7a** and the racemate **7b**/**7c** (*Z*-isomer). Obviously, the existence of three analogous stereoisomer forms (**6a—c**) should already be suggested at the level of the initial azine **6** as the result of substitution at the geminal position of $C_{2h}$-symmetric molecule **4** with different (namely, CH$_3$- and CCl$_3$-)

**Scheme 1**



**Reagents and conditions:** *a*. 1/2 N$_2$H$_4$·H$_2$O, EtOH, 5 h, 70 °C; *b*. 2 (Na$_2$PdCl$_4$·3H$_2$O), THF, 5 h, 70—75 °C; *c*. excess (acacH/KOH), THF, 24 h, 20 °C.

groups. Thus, our reaction is of interest from the stereochemical point of view. It offers a fundamentally new route to the synthesis of very rare chiral organometallic compounds of the type **7b**, **c** with rotational symmetry.

The importance of the reaction discovered, which we are continuing to study for the *ortho*-semiquinoid system (6,6-disubstituted 2,4-cyclohexadienone azines) and the corresponding quinoid ligands (*ortho*- and *para*-quinonazines), is that it involves the organometallic activation of the C—H bonds in the inert 2-positions of cyclohexadienylidene rings with possible subsequent functionalization of the polyheteroelemental synthons of this new class.

## Experimental

The course of the reaction was monitored by TLC on a Silufol UV-254 plates. Spots were detected under ultraviolet light. $^1$H NMR spectra were recorded on a Bruker AMX 400 spectrometer, using the signals of the residual protons from deuterated solvents as internal standards. All reactions were carried out under an argon atmosphere.

Azine **6**[9] (mixture of stereoisomers) and $Na_2PdCl_4$[10] were prepared by the known procedures. Acetylacetone was distilled before use; the solvents were dried using the standard procedures.

**Reaction of 4-methyl-4-trichlormethylcyclohexa-2,5-dien-1-one azine(6) with $Na_2PdCl_4 \cdot 3H_2O$.** A suspension of 0.048 g of azine **6** (0.108 mmol) and 0.075 g of $Na_2PdCl_4 \cdot 3H_2O$ (0.217 mmol) in 4 ml of THF was stirred at 20 °C for 10 minutes, then heated at 70—75 °C for 5 h, cooled, and kept at 20 °C for 48 h. The dark green precipitate that formed was filtered off, washed with THF (4 mL) and $H_2O$ (35 mL) until the chloride ions in the filtrate disappeared, and dried *in vacuo* over $P_2O_5$ to give 0.033 g of the complex. Then, 0.008 g (0.082 mmol) of acetylacetone and 0.0046 g (0.082 mmol) of KOH were added to a suspension of 0.022 g (0.027 mmol) of the complex obtained in 2 mL of THF, and the resulting mixture was stirred at 20 °C for 24 h. The solvent was evaporated, the residue was extracted with $C_6H_6$ (4 mL), the extract was filtered, and the filtrate was evaporated to give 0.02 g (37.7%) of a mixture of two diastereoisomers ($R_f = 0.6$ and 0.83 ($C_6H_6$)) of 5,10-bis(acetylacetonato)2,7-dimethyl-2,7-bis(trichloromethyl)-2,7-dihydro-4b,9b-diaza-5,10-dipalladaindeno[2,1-*a*]indene (**7*a*—*c***) in the form of a yellow microcrystalline powder. Found (%): C, 35.80; H, 2.38; N, 3.35. $C_{26}H_{26}Cl_6N_2O_4Pd_2 \cdot H_2O$. Calculated (%): C, 35.73; H, 3.23; N, 3.21. To enrich the mixture obtained with one of the stereoisomers (with higher solubility), the mixture was extracted with $Et_2O$ (10 mL) and the ethereal extract was concentrated to 2—3 mL and left overnight at 10 °C. The crystals that precipitated (fraction *A*, 0.001 g), which are of deeper color (with an orange shade) than the initial mixture of diastereoisomers, were decanted and dried *in vacuo*. The residue insoluble in ether (fraction *B*; 0.0073 g) and of a lighter (pure yellow) shade was dried, and both fractions thus obtained were compared by $^1$H NMR.

$^1$H NMR spectrum of fraction *A* ($CD_2Cl_2$, δ; the signals of the main (orange) stereoisomer are marked by an asterisk): 1.59 (s, $CH_{3gem}$); 1.601* (s, $CH_{3gem}$); 2.00 (s, $CH_{3acac}$); 2.005 (s, $CH_{3acac}$); 5.41 (s, $CH_{acac}$); 6.703* (d, $H_x$, $^4J = 2.6$ Hz); 6.712 (d, CH, $^4J = 2.6$ Hz); 7. 00 (dd, $CH_B$, $^3J = 10.2$ Hz, $^4J = 2.6$ Hz); 8.28 (d, $CH_A$, $^3J = 10.2$ Hz). $^1$H NMR spectrum of fraction *A* ($C_6D_6$), δ: 1.375 (s, $CH_{3gem}$); 1.38* (s, $CH_{3gem}$); 1.79 (s, $CH_{3acac}$); 1.82* (s, $CH_{3acac}$); 5.202 (s, $CH_{acac}$); 5.205* (s, $CH_{acac}$); 6.83 (dd, $CH_B$, $^3J = 10.1$ Hz, $^4J = 2.5$ Hz); 6.84* (dd, $CH_B$, $^3J = 10.1$ Hz, $^4J = 2.5$ Hz); 8.59 (d, $CH_A$, $^3J = 10.1$ Hz); 8.6* (d, $CH_A$, $^3J = 10.1$ Hz). According to the areas of the corresponding resonance peaks in the spectrum, the observed ratio of stereoisomers is 3 : 1.

$^1$H NMR spectrum of fraction *B* ($CD_2Cl_2$, δ; the signals of the orange stereoisomer are marked by an asterisk): 1.597 (s, $CH_{3gem}$); 1.601* (s, $CH_{3gem}$); 2.00 (s, $CH_{3acac}$); 2.005 (s, $CH_{3acac}$); 5.41 (s, $CH_{acac}$); 6.703* (d, $CH_x$, $^4J = 2.6$ Hz); 6.712 (d, $CH_x$, $^4J = 2.6$ Hz); 7.00 (dd, $CH_B$, $^3J = 10.2$ Hz, $^4J = 2.6$ Hz); 8.28 (d, $CH_A$, $^3J = 10.2$ Hz). $^1$H NMR spectrum of fraction *B* ($C_6D_6$), δ: 1.375 (s, $CH_{3gem}$); 1.38* (s, $CH_{3gem}$); 1.79 (s, $CH_{3acac}$); 1.82 (s, $CH_{3acac}$); 5.202 (s, $CH_{acac}$); 5.205* (s, $CH_{3acac}$); 6.83 (dd, $CH_B$, $^3J = 10.1$ Hz, $^4J = 2.5$ Hz); 6.84* (dd, $CH_B$, $^3J = 10.1$ Hz, $^4J = 2.5$ Hz); 8.59 (d, $CH_A$, $^3J = 10.1$ Hz); 8.6* (d, $CH_A$, $^3J = 10.1$ Hz). The observed ratio of stereoisomers is 1 : 1.

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