by using a cannula according to standard Schlenk procedure.

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Registry No. $Pd(OAc)_2(PPh_3)_2$, 14588-08-0; $Pd(PPh_3)_2$, 31989-57-8; $PhPd^{II}I(PPh_3)_2$, 55123-60-9; $Pd(PPh_3)_4$, 14221-01-3; $POPh_3$, 791-28-6; $PhPdOAc(PPh_3)_2$, 56925-72-5; $Pd(PPh_3)_3$, 28516-49-6.

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Cyclometalation of *N*-(4-Methoxyphenyl)-α-benzoylbenzylideneamine with Palladium(II) Acetate. Evidence for a New Kind of Diastereoisomerism

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The reaction of $Pd(OAc)_2$ with *N*-(4-methoxyphenyl)-α-benzoylbenzylideneamine yielded two different acetate-bridged ortho-palladated compounds, $Pd_2[4\text{-}OCH_3C_6H_4N{=}C(COC_6H_5)C_6H_5]_2(\mu\text{-}OAc)_2$ (**2** and **3**), depending on the relative ratio of the reagents. Both diastereoisomeric complexes exhibit a nonplanar, open-book shape, differing only in the dihedral angle formed between the $C_6H_5C{=}O$ and the $C_6H_5C{=}N$ planes; i.e., they are atropisomers around the CO–CN bond, as could be established from X-ray diffraction data. Both complexes crystallize in the centrosymmetric triclinic space group $P\bar{1}$, with $Z = 2$. Unit cell parameters are as follows: compound **2**, $a = 14.206$ (9) Å, $b = 15.764$ (5) Å, $c = 11.149$ (3) Å, $\alpha = 92.46$ (2)°, $\beta = 95.31$ (4)°, $\gamma = 116.03$ (4)°; compound **3**, $a = 11.889$ (15) Å, $b = 13.209$ (23) Å, $c = 15.436$ (9) Å, $\alpha = 87.34$ (1)°, $\beta = 78.51$ (7)°, $\gamma = 87.73$ (1)°.

Introduction

The ortho-palladation reaction of benzylamines and related derivatives is a well-known process. Also, the characteristic form of the complexes resulting from these reactions is known.[1] Of special interest are those dimers containing two palladium centers linked by two bridging acetate groups. In these cases, the acetate groups can force the two square planes of each palladium atom to have a relatively small dihedral angle,[2] resulting in the molecule adopting a nonplanar open-book shape. This configuration does not undergo inversion under literature conditions[3] (opposite to the fluxionality observed in other complexes exhibiting an open-book structure in the solid state[4]), and therefore, the complexes are chiral. This new kind of chirality has been postulated from NMR studies on carboxylato-bridged ortho-palladated azines containing a chiral center at the carboxylated moiety.[5]

The benzoylbenzylideneamines prepared from chiral nonracemic amines exhibit mutarotation in several solvents.[6] This fact was explained by assuming an equilibrium between the atropisomers A and B (Figure 1), resulting from the restricted rotation around the CO–CN bond, which becomes a chiral axis. Nevertheless, this proposal, which was based on kinetic considerations,[7] was never unequivocally demonstrated because of the inability to isolate each atropisomer, probably due to the low activation energy for rotation.

The interest in these compounds as ligands derives from the different adducts which can be formed, depending on the size of the cyclometalated ring,[8] the nature of the heteroatom involved (oxygen or nitrogen), or the stereochemistry (cis or trans) adopted for the two imine molecules involved in the dinuclear species which must presumably be formed. There is another factor related to the open-book shape of the complexes, which suggests the possibility of increasing the activation energy for rotation around the CO–CN bond sufficiently, to allow the isolation of the atropisomers, which would afford unambiguous evidence for both chiral axes (the CO–CN bond and the spine of the book).

We herein report the synthesis, spectroscopic characterization, and X-ray diffraction data for the two atropisomeric complexes resulting from the reactions of Pd(O-

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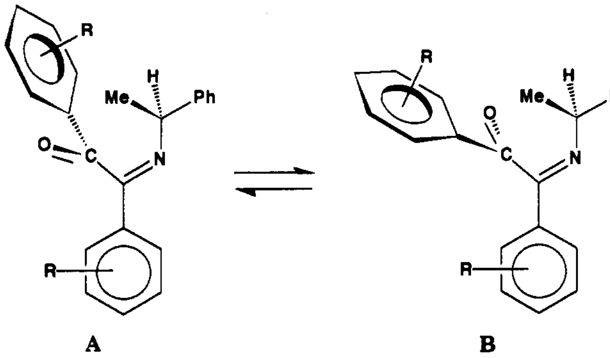

Figure 1.

Ac)$_2$ with *N*-(4-methoxyphenyl)-α-benzoylbenzylideneamine.

Results and Discussion

Synthesis and Characterization of the Complexes. The reaction between $[Pd(OAc)_2]_3$ (1 equiv) and the imine $4\text{-}OCH_3C_6H_4N{=}C(COC_6H_5)C_6H_5$ (1; 2 equiv), in refluxing glacial AcOH under nitrogen for 2 h, afforded the orange complex 2 in 76% yield. When the same reaction was carried out using identical amounts of both reagents, a different orange complex, 3, was isolated in 36% yield. Both compounds were easily separated and purified by chromatography.[9]

The microanalytical data for 2 and 3 (see (Experimental Section) are consistent with the same empirical formula, $C_{23}H_{19}NO_4Pd$, which indicates the structure [LPdAc]. The IR spectra show two bands at ca. 1580 and 1420 cm^{-1}, which are typical of bridging acetates[10] and suggest that both complexes are dimers, $[LPdAc]_2$. The C=O stretching absorptions appearing at ca. 1670 cm^{-1} in ligand 1 and complexes 2 and 3 indicate that the carbonyl group cannot be involved in Pd coordination. The C=N stretching absorptions appear 17–21 cm^{-1} lower in complexes 2 and 3 (1606 and 1602 cm^{-1}) than in ligand 1 (1623 cm^{-1}), which suggests that the N lone pair must be involved in coordination.[1b]

The ^{1}H NMR signals of 2 and 3 are broadened, even at 80 °C. Both spectra are similar, making it impossible to differentiate the complexes. Remarkably, both exhibit only one signal for the acetate methyl group at δ 1.59 ppm (which suggests a trans disposition of ligands[11]). This chemical shift can be considered a normal value for an acetate complex derived from phenyl ketimines,[3,12] despite the fact that it represents an upfield shift compared to that of $[Pd(OAc)_2]_3$ (δ 2.05 ppm). This shielding, as well as the broadening of the signals, could be due to the spatial arrangement of the aromatic rings in these complexes.

The ^{13}C NMR parameters of ligand 1 and complexes 2 and 3 are collected in Table I. Since the reports concerning the ^{13}C NMR data for these complexes are scarce in the literature, it was necessary to carry out a detailed study of these spectra.

In ligand 1, the assignment of carbons C1–C12 (coming from the starting benzil) was made on the basis of the data reported for other similar benzoylbenzylideneamines.[13] The signals corresponding to the *p*-methoxyphenyl ring were assigned by comparison with other *N*-*p*-methoxyphenyl imines.[14] These assignments were reinforced by heteronuclear correlation two-dimensional NMR spectroscopy.

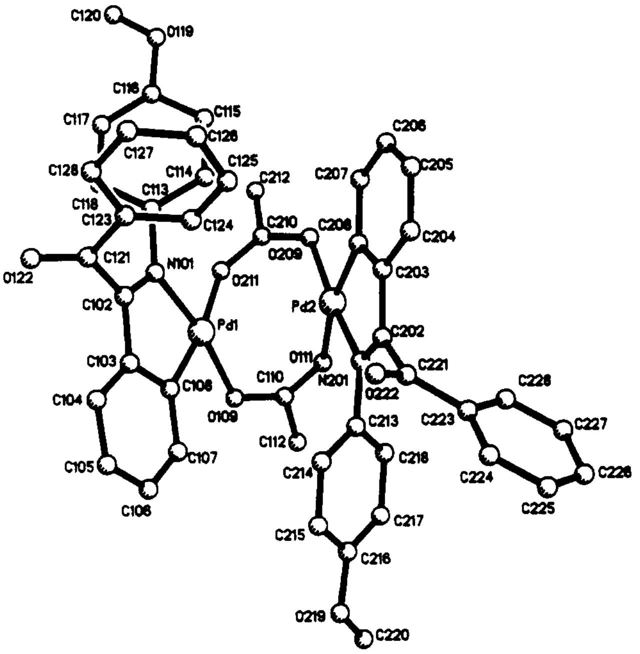

Figure 2. Molecular structure of 2 showing the atom-numbering scheme. H atoms have been omitted for clarity (compound 3 is similar, with atoms denoted by primes).

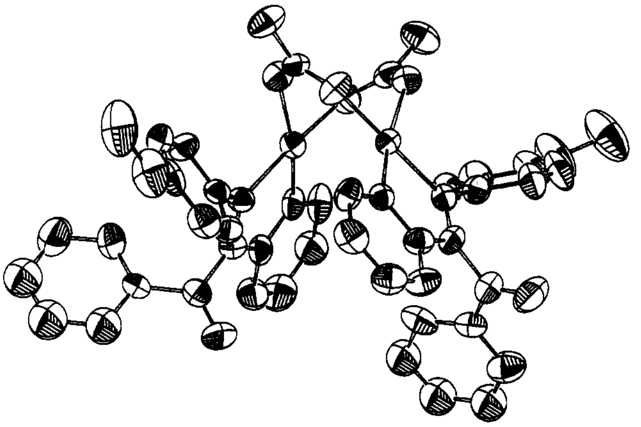

Figure 3. ORTEP drawing (50% ellipsoid level) of the molecular structure of 2.

For complexes 2 and 3, the carbon assignments were carried out by taking into account the values observed for the ligand and those of other monomeric cyclopalladated compounds[15] derived from *N*-4-methoxyphenyl-α-benzoylbenzylideneamine. The effect of cyclopalladation on chemical shifts of the aromatic protonated carbons is in accord with those reported[16] for other cyclopalladated

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[9] In both cases, the chromatographic separation allowed us to isolate a minor product (<10%), a third diastereoisomer whose structure is being investigated.

[10] Nakamoto, K. *IR and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-Interscience: New York, 1978; p 232.

[11] If both ligands adopt a cis disposition, the two bridging acetate methyl groups would have different chemical environments and, consequently, should appear as two singlets.

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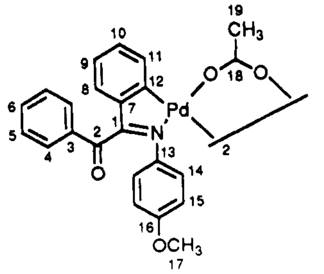
[15] Unpublished results. We have also carried out the heteronuclear correlation two-dimensional NMR spectroscopy of 2 and 3; the broadening of the signals in the proton spectra reduces our confidence in the conclusions based on this technique.

Table I. ^{13}C NMR Parameters (δ, ppm) of the Ligand 1 and Those of the Complexes 2 and 3 in CD_2Cl_2



carbon	compd 1	compd 2	compd 3
C1	165.6	180.5	180.5
C2	198.8	202.4	193.0
C3	134.8	NO[a]	NO
C4,4′	129.1	129.5	129.5
C5,5′	128.2	129.5	129.5
C6	134.8	135.2	135.2
C7	135.7	146.1	146.2
C8	129.3	128.3	128.3
C9	129.5	124.7	124.7
C10	131.8	131.4	131.4
C11	129.5	133.8	133.7
C12	129.3	156.4	156.5
C13	142.7	138.4	138.5
C14,14′	122.5	126.2	126.2
C15,15′	114.2	113.2	113.2
C16	157.5	159.0	159.0
C17	55.5	55.7	55.7
C18		NO	NO
C19		24.0	24.0

[a] NO = not observed.

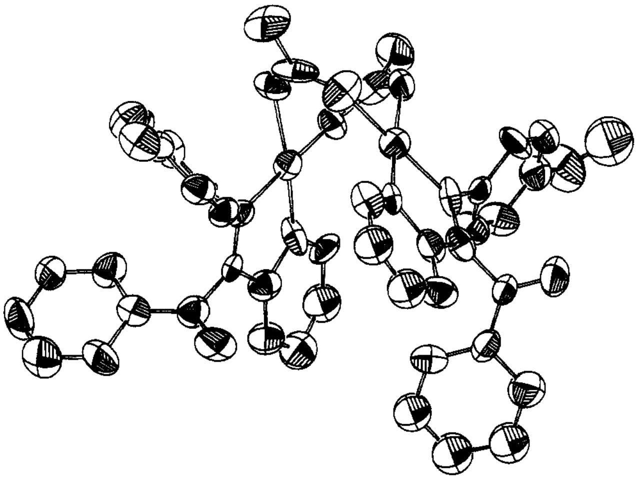


Figure 4. ORTEP drawing (50% ellipsoid level) of the molecular structure of 3.

compounds derived from *N*-phenylbenzylideneamine. In ref 16, there is no mention of quaternary deprotonated carbons, which should be the most affected by cyclopalladation. Thus, C12, which is directly joined to the palladium, is strongly deshielded ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ = 27.2 ppm). The effect of the metal on those carbons in β-positions is different, depending on their nature (Δδ(C13) = −4.3, Δδ(C7) = +10.4, Δδ(C1) = +14.9, and Δδ(C11) = +4.3 ppm). Extensive elaboration will appear elsewhere.

The only significant difference between the ^{13}C NMR spectra of 2 and 3 is the chemical shift of carbonyl C2, which differs by 9.4 ppm. This difference must be due to the distinct anisotropic effects of the rings on each carbonyl group as a consequence of its spatial arrangement into the folded shape of each complex.

Table II. Positional Parameters and U_{eq} Values for the Non-Hydrogen Atoms and Their Estimated Standard Deviations for Compound 2

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Pd1	0.8987 (1)	0.1715 (1)	0.5529 (1)	40 (1)
N101	0.8425 (7)	0.0539 (6)	0.4340 (7)	40 (4)
C102	0.7480 (9)	−0.0098 (8)	0.446 (1)	48 (5)
C103	0.6974 (9)	0.0138 (8)	0.541 (1)	50 (5)
C104	0.5983 (9)	−0.0470 (9)	0.570 (1)	60 (6)
C105	0.558 (1)	−0.016 (1)	0.661 (1)	65 (6)
C106	0.615 (1)	0.073 (1)	0.720 (1)	65 (6)
C107	0.715 (1)	0.1327 (8)	0.694 (1)	52 (5)
C108	0.7575 (8)	0.1046 (7)	0.6016 (9)	40 (5)
O109	0.9417 (7)	0.2757 (6)	0.6925 (7)	58 (4)
C110	0.9874 (8)	0.3624 (8)	0.677 (1)	48 (5)
O111	0.9972 (6)	0.3966 (5)	0.5789 (7)	53 (4)
C112	1.026 (1)	0.4286 (9)	0.791 (1)	71 (7)
C113	0.9036 (9)	0.0368 (8)	0.348 (1)	48 (5)
C114	0.9335 (9)	0.0993 (9)	0.258 (1)	52 (5)
C115	0.995 (1)	0.089 (1)	0.177 (1)	70 (7)
C116	1.029 (1)	0.020 (1)	0.187 (1)	76 (8)
C117	0.999 (1)	−0.040 (1)	0.273 (1)	80 (9)
C118	0.934 (1)	−0.034 (1)	0.357 (1)	63 (7)
O119	1.0938 (9)	0.0182 (9)	0.1017 (9)	111 (7)
C120	1.150 (1)	−0.032 (1)	0.120 (1)	126 (11)
C121	0.690 (1)	−0.0990 (8)	0.362 (1)	64 (6)
O122	0.6725 (8)	−0.1746 (6)	0.3978 (9)	82 (5)
C123	0.6549 (8)	−0.0885 (8)	0.236 (1)	51 (5)
C124	0.6644 (9)	−0.002 (1)	0.200 (1)	64 (6)
C125	0.6269 (9)	0.0031 (8)	0.081 (1)	76 (3)
C126	0.5850 (9)	−0.0733 (8)	0.003 (1)	83 (3)
C127	0.5737 (9)	−0.1594 (8)	0.035 (1)	80 (3)
C128	0.608 (1)	−0.169 (1)	0.154 (1)	76 (7)
Pd2	0.9245 (1)	0.3351 (1)	0.4017 (1)	42 (1)
N201	0.7856 (6)	0.3408 (6)	0.4136 (8)	42 (4)
C202	0.7252 (9)	0.3225 (8)	1.313 (1)	48 (5)
C203	0.767 (1)	0.3017 (8)	0.207 (1)	47 (5)
C204	0.717 (1)	0.288 (1)	1.087 (1)	64 (7)
C205	0.765 (1)	0.274 (1)	−0.005 (1)	78 (8)
C206	0.8622 (9)	0.2757 (8)	0.017 (1)	68 (3)
C207	0.914 (1)	0.2894 (8)	0.132 (1)	61 (6)
C208	0.8663 (9)	0.3042 (7)	0.232 (1)	48 (5)
O209	1.0572 (6)	0.3257 (6)	0.3649 (7)	57 (4)
C210	1.0960 (9)	0.2784 (8)	0.423 (1)	50 (5)
O211	1.0563 (6)	0.2275 (5)	0.5061 (7)	54 (4)
C212	1.199 (1)	0.284 (1)	0.390 (1)	79 (8)
C213	0.7513 (8)	0.3588 (8)	1.5255 (9)	41 (5)
C214	0.6585 (8)	0.2910 (8)	0.560 (1)	51 (5)
C215	0.627 (1)	0.311 (1)	1.666 (1)	64 (7)
C216	0.683 (1)	0.393 (1)	1.738 (1)	64 (7)
C217	0.775 (1)	0.4603 (9)	1.703 (1)	61 (6)
C218	0.8099 (9)	0.4423 (8)	1.595 (1)	53 (5)
O219	0.644 (1)	0.4022 (9)	0.8419 (9)	98 (7)
C220	0.700 (1)	0.481 (1)	0.921 (1)	117 (8)
C221	0.6171 (9)	0.3194 (8)	0.301 (1)	52 (5)
O222	0.5411 (7)	0.2440 (6)	0.275 (1)	80 (5)
C223	0.6080 (9)	0.4095 (8)	0.315 (1)	56 (5)
C224	0.5097 (9)	0.4077 (8)	0.321 (1)	80 (3)
C225	0.5018 (9)	0.4914 (8)	0.332 (1)	93 (3)
C226	0.5839 (9)	0.5746 (8)	0.334 (1)	90 (3)
C227	0.685 (1)	0.580 (1)	0.327 (1)	93 (7)
C228	0.696 (1)	0.496 (1)	0.319 (1)	72 (7)
O1	0.120 (1)	0.269 (1)	0.920 (1)	127
C2	0.206 (4)	0.245 (3)	0.955 (4)	290
C3	0.293 (2)	0.273 (2)	1.060 (2)	138

[a] $U_{eq} = {}^1/_3|\sum(U_{ij}a_i{}^*a_j{}^*a_ia_j[\cos(a_i,a_j)]| \times 10^3$.

X-ray studies of single crystals of 2 and 3 were made to confirm their structures. The scheme used for labeling atoms in the complexes is shown in Figure 2. ORTEP drawings of the molecules based on the X-ray structural analyses are shown in Figures 3 (complex 2) and 4 (complex 3). Atomic parameters for the non-hydrogen atoms are listed in Tables II and III. Significant bond distances and bond angles are listed in Tables IV and V.

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Table III. Positional Parameters and U_{eq} Values for the Non-Hydrogen Atoms and Their Estimated Standard Deviations for Compound 3

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Pd1′	−0.0137 (1)	0.8259 (1)	0.7123 (1)	54 (8)
N101′	−0.151 (1)	0.809 (1)	0.6621 (9)	50 (6)
C102′	−0.189 (2)	0.713 (2)	0.669 (1)	52 (7)
C103′	−0.119 (2)	0.641 (2)	0.710 (1)	59 (8)
C104′	−0.145 (2)	0.537 (2)	0.720 (2)	72 (9)
C105′	−0.072 (3)	0.476 (2)	0.761 (2)	86 (8)
C106′	0.019 (3)	0.510 (3)	0.785 (2)	87 (8)
C107′	0.040 (2)	0.616 (2)	0.773 (1)	69 (9)
C108′	−0.022 (2)	0.681 (2)	0.741 (1)	68 (9)
O109′	0.136 (1)	0.825 (1)	0.757 (1)	75 (6)
C110′	0.151 (2)	0.888 (2)	0.816 (2)	70 (10)
O111′	0.082 (1)	0.936 (1)	0.860 (1)	61 (5)
C112′	0.274 (2)	0.891 (2)	0.829 (2)	91 (10)
C113′	−0.216 (2)	0.887 (1)	0.620 (1)	44 (6)
C114′	−0.156 (2)	0.934 (2)	0.544 (1)	72 (9)
C115′	−0.216 (2)	1.008 (2)	0.503 (1)	66 (9)
C116′	−0.325 (2)	1.036 (2)	0.538 (2)	67 (9)
C117′	−0.381 (2)	0.989 (2)	0.615 (2)	70 (9)
C118′	−0.326 (2)	0.912 (2)	0.655 (1)	64 (8)
O119′	−0.385 (2)	1.106 (2)	0.499 (2)	105 (9)
C120A[b]	−0.359 (5)	1.129 (6)	0.419 (4)	134 (15)
C120B[b]	−0.357 (9)	1.19 (1)	0.437 (8)	133 (23)
C121′	−0.292 (2)	0.683 (2)	0.632 (1)	57 (8)
O122′	−0.274 (2)	0.674 (2)	0.551 (1)	94 (9)
C123′	−0.402 (2)	0.660 (2)	0.690 (1)	58 (8)
C124′	−0.492 (3)	0.622 (2)	0.655 (2)	84 (11)
C125′	−0.592 (3)	0.596 (3)	0.710 (2)	91 (8)
C126′	−0.609 (3)	0.613 (3)	0.799 (2)	95 (8)
C127′	−0.523 (3)	0.650 (2)	0.834 (2)	81 (7)
C128′	−0.419 (2)	0.670 (2)	0.780 (2)	60 (8)
Pd2′	−0.1001 (1)	0.9167 (1)	0.8832 (1)	48 (1)
N201′	−0.098 (1)	0.802 (1)	0.975 (1)	44 (5)
C202′	−0.205 (2)	0.774 (2)	1.015 (1)	55 (7)
C203′	−0.301 (2)	0.821 (2)	0.982 (1)	57 (7)
C204′	−0.413 (2)	0.801 (2)	1.009 (2)	74 (9)
C205′	−0.497 (2)	0.849 (2)	0.973 (2)	80 (10)
C206′	−0.466 (3)	0.936 (2)	0.916 (2)	82 (8)
C207′	−0.351 (2)	0.954 (2)	0.881 (1)	59 (8)
C208′	−0.264 (2)	0.903 (2)	0.915 (1)	61 (8)
O209′	−0.121 (1)	1.035 (1)	0.8017 (9)	51 (5)
C210′	−0.063 (2)	1.049 (1)	0.720 (2)	55 (8)
O211′	−0.008 (1)	0.983 (1)	0.6764 (8)	51 (5)
C212′	−0.075 (3)	1.152 (2)	0.677 (2)	88 (10)
C213′	0.001 (1)	0.762 (1)	1.004 (1)	42 (6)
C214′	0.031 (2)	0.662 (1)	0.989 (1)	51 (7)
C215′	0.133 (2)	0.620 (2)	1.010 (1)	59 (7)
C216′	0.200 (2)	0.682 (1)	1.046 (1)	54 (7)
C217′	0.169 (2)	0.783 (2)	1.065 (1)	59 (8)
C218′	0.067 (2)	0.825 (2)	1.039 (1)	62 (8)
O219′	0.303 (1)	0.651 (1)	1.072 (1)	72 (6)
C220′	0.337 (2)	0.547 (2)	1.063 (2)	80 (10)
C221′	−0.225 (2)	0.694 (2)	1.092 (1)	60 (8)
O222′	−0.240 (2)	0.607 (1)	1.075 (1)	82 (7)
C223′	−0.231 (2)	0.731 (2)	1.179 (1)	54 (7)
C224′	−0.204 (2)	0.827 (2)	1.196 (2)	68 (9)
C225′	−0.212 (2)	0.856 (2)	1.284 (1)	70 (9)
C226′	−0.250 (2)	0.788 (2)	1.352 (1)	86 (10)
C227′	−0.271 (3)	0.692 (2)	1.336 (2)	89 (11)
C228′	−0.268 (3)	0.659 (2)	1.251 (2)	83 (10)

[a] $U_{eq} = {}^1/_3|\sum(U_{ij}a_i{}^*a_j{}^*a_ia_j[\cos(a_i,a_j)]| \times 10^3$. [b] C120′ atom in a disordered position, with the occupancy factor *ij* equal to 0.65 in the first position.

The structures of both complexes contain discrete dimeric molecules without any element of symmetry. Each palladium atom is bonded to four atoms—the nitrogen, the ortho carbon atom of the phenyl ring supporting the iminic carbon, and one oxygen atom from each of the two bridging acetates—in a distorted-square-planar coordination approaching tetrahedral geometry. The dihedral angles between planes N–Pd–C and O–Pd–O for Pd1 and Pd2 (complex 2) are 9.1 (3)° and 11.2 (4)°, respectively. The angles for Pd1′ and Pd2′ (complex 3) are 5.1 (7)° and 6.2 (6)°, respectively. Although most crystal structures of cyclopalladated complexes have shown a square-planar coordination geometry,[17] recent examples have described tetrahedral distortions about the palladium atom,[18] due probably to the folded open-book shape. The Pd–N and Pd–C bonds form the basis for a five-membered chelate ring. The Pd–N bond lengths (Pd1–N101 = 2.031 (8) Å and Pd2–N201 = 2.03 (1) Å in **2**; Pd1′–N101′ = 1.97 (2) Å and Pd2′–N201′ = 2.02 (1) Å in **3**) are in reasonable agreement with the predicted value of 2.01 Å (based upon

Table IV. Selected Bond Distances and Angles for Compound 2

Distances (Å)			
Pd1–N101	2.031 (8)	Pd2–N201	2.03 (1)
Pd1–C108	1.95 (1)	Pd2–C208	1.95 (1)
Pd1–O109	2.054 (8)	Pd2–O209	2.03 (1)
Pd1–O211	2.141 (8)	Pd2–O111	2.119 (7)
N101–C102	1.30 (1)	N201–C202	1.29 (1)
C102–C103	1.45 (2)	C202–C203	1.45 (2)
C102–C121	1.51 (1)	C202–C221	1.51 (2)
C103–C108	1.40 (1)	C203–C208	1.40 (2)
O109–C110	1.26 (1)	O209–C210	1.27 (2)
C110–O111	1.23 (1)	C210–O211	1.26 (1)
C110–C112	1.51 (1)	C210–C212	1.50 (2)
C121–O122	1.20 (2)	C221–O222	1.20 (1)
C121–C123	1.48 (2)	C221–C223	1.48 (2)
Pd1–Pd2	3.046 (2)		
Angles (deg)			
O109–Pd1–O211	92.1 (4)	O209–Pd2–O111	90.2 (4)
C108–Pd1–O109	91.3 (4)	C208–Pd2–O209	91.2 (5)
N101–Pd1–O211	94.7 (4)	N201–Pd2–O111	97.4 (4)
N101–Pd1–C108	81.1 (4)	N201–Pd2–C208	81.0 (5)
Pd1–N101–C102	114.9 (8)	Pd2–N201–C202	115.1 (8)
N101–C102–C103	116 (1)	N201–C202–C203	115 (1)
C102–C103–C108	114 (1)	C202–C203–C208	114 (1)
Pd1–C108–C103	114.0 (9)	Pd2–C208–C203	114.2 (8)

Table V. Selected Bond Distances and Angles for Compound 3

Distances (Å)			
Pd1′–N101′	1.97 (2)	Pd2′–N201′	2.02 (1)
Pd1′–C108′	1.94 (3)	Pd2′–C208′	1.93 (2)
Pd1′–O109′	2.03 (2)	Pd2′–O209′	2.00 (1)
Pd1′–O211′	2.12 (1)	Pd2′–O111′	2.14 (2)
N101′–C102′	1.34 (3)	N201′–C202′	1.35 (3)
C102′–C103′	1.44 (3)	C202′–C203′	1.45 (3)
C102′–C121′	1.53 (4)	C202′–C221′	1.55 (3)
C103′–C108′	1.46 (4)	C203′–C208′	1.47 (3)
O109′–C110′	1.30 (4)	C209′–C210′	1.31 (3)
C110′–O111′	1.15 (3)	C210′–O211′	1.22 (2)
C110′–C112′	1.53 (3)	C210′–C212′	1.50 (3)
C121′–O122′	1.22 (3)	C221′–O222′	1.21 (3)
C121′–C123′	1.46 (3)	C221′–C223′	1.44 (3)
Pd1′–Pd2′	2.927 (3)		
Angles (deg)			
O109′–Pd1′–O211′	93.8 (7)	O209′–Pd2′–O111′	91.6 (6)
C108′–Pd1′–O109′	88.6 (9)	C208′–Pd2′–O209′	90.5 (8)
N101′–Pd1′–O211′	92.4 (6)	N201′–Pd2′–O111′	94.4 (7)
N101′–Pd1′–C108′	85 (1)	N201′–Pd2′–C208′	83.2 (8)
Pd1′–N101′–C102′	114 (1)	Pd2′–N201′–C202′	113 (1)
N101′–C102′–C103′	114 (2)	N201′–C202′–C203′	117 (2)
C102′–C103′–C108′	116 (2)	C202′–C203′–C208′	112 (2)
Pd1′–C108′–C103′	110 (2)	Pd2′–C208′–C203′	114 (2)

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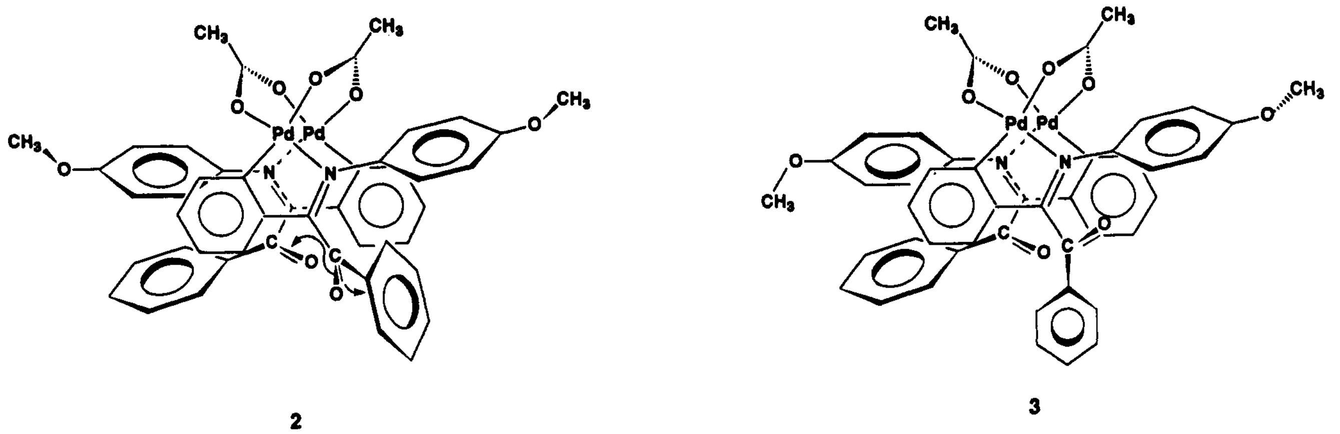

2

3

Figure 5. Different spatial arrangements of the benzoyl groups in compounds 2 and 3.

r(Pd(II)) = 1.31 Å and r(N) = 0.70 Å[19]). However, all Pd–C bond lengths (Pd1–C108 = 1.95 (1) Å and Pd2–C208 = 1.95 (1) Å in 2 and Pd1′–C108′ = 1.94 (3) Å and Pd2′–C208′ = 1.93 (2) Å in 3) are substantially shorter than the predicted value of 2.05 Å[20] but are similar to those in other aryl complexes.[18a] This suggests some multiple-bond character in Pd–C linkages due to metal-to-ligand back-bonding,[18a,21] a conclusion which is supported by the NMR data.

The Pd–O bonds having nitrogen atoms in a trans position are significantly shorter (2 Pd1–O109 = 2.054 (8) Å and Pd2–O209 = 2.03 (1) Å; 3, Pd1′–O109′ = 2.03 (2) Å and Pd2′–O209′ = 2.00 (1) Å) than those showing a trans relationship with respect to the aromatic carbon (2, Pd1–O211 = 2.141 (8) Å and Pd2–O111 = 2.119 (7) Å; 3, Pd1′–O211′ = 2.12 (1) Å and Pd2′–O111′ = 2.14 (2) Å), as a consequence of the different trans influences of both atoms.[22] All distances and angles within the acetate and the aromatic groups are normal.

Pd–Pd distances of 3.046 (2) Å in 2 and 2.927 (3) Å in 3 are in the range observed for the other Pd complexes in which metal–metal interactions have been postulated.[23]

Iminic and carbonyl groups retain an almost orthogonal arrangement as exhibited in N-substituted 1-benzoylbenzylideneamines.[24] The main difference between 2 and 3 is in the torsion angles, which exhibit values for N101–C102–C121–O122 and N201–C202–C221–O222 of 112 (1) and –111 (1)° for 2 and 75 (3) and –96 (3)° for 3. In Figure 5, the main spatial differences between the structures of the complexes are depicted. They differ in the conformation around the CO–CN bond of one of the ligands with respect to the other. Therefore, complexes 2 and 3 are atropisomers.[25]

We suspect that the strong steric effects in the boatlike conformation of these metalated dimers are the main reason for the hindered rotation about the OC–CN bond, which becomes a chiral axis, making possible the existence of both diastereoisomeric complexes 2 and 3. Interligand repulsions lead to the molecule "opening up" on the side opposite the μ-acetato systems. The PdOONC planes are 42.73° in 2 and 37.47° in 3, which are larger than in other cyclometalated compounds with acetate ligands (24.46 and 23.96° when the ligands are benzothiazole and benzoxazole, respectively).[17a]

Experimental Section

The infrared spectra were recorded in Nujol mulls and KBr pellets in the 4000–200-cm^{-1} range with a Perkin-Elmer Model 283 spectrophotometer. NMR spectra were recorded on a Bruker WP-200-SY (200-MHz) spectrometer in CD_2Cl_2, with TMS as internal standard. The C, H, and N analyses were was carried out with a Perkin-Elmer 240B microanalyzer.

All solvents were purified, prior to use, by the standard methods.[26] Palladium(II) acetate was purchased from Merck. The ligand synthesis follows published methods.[27]

Synthesis of Complexes 2 and 3. In a 100-mL round-bottomed flask, 630 mg (2 mmol) of 1 and 220 mg (1 mmol) of palladium(II) acetate were added to 12 mL of glacial AcOH under N_2 at 50 °C. After 2 h, the clear solution was cooled, diluted with water, and extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude residue was column-chromatographed (SiO_2) with CH_2Cl_2 as eluent to remove any unchanged starting materials. Upon further elution with CH_2Cl_2–EtOH (99:1), two separate bands became visible, yielding the orange complex 2 (76% yield) a yellow complex (10% yield) of unknown structure. When the reaction was carried out under identical conditions, but using equimolar amounts of ligand and palladium(II) acetate, in addition to the yellow unknown (9% yield), the complex 3 (36% yield) was isolated.

Complex 2. Anal. Calcd: C, 57.58; H, 3.99; N, 2.92. Found: C, 57.60; H, 3.99; N, 2.95. ^{1}H NMR: δ (ppm) 7.75–6.80 (m, 9 H), 6.75 and 6.63 (AA′BB′, 4 H), 3.69 (s, 3 H), 1.59 (s, 3 H). IR: ν_{max} 1670, 1606, 1580, 1420 cm^{-1}.

Complex 3. Anal. Calcd: C, 57.58; H, 3.99; N, 2.92. Found: C, 57.54; H, 3.95; N, 2.90. ^{1}H NMR: δ (ppm) 7.75–6.80 (m, 9 H), 6.75 and 6.63 (AA′BB′, 4 H), 3.69 (s, 3 H), 1.59 (s, 3 H). IR: ν_{max} 1671, 1602, 1580, 1420 cm^{-1}.

Structure Determination and Refinement of Complex 2. Recrystallization by slow evaporation from a CH_2Cl_2–EtOH (99:1) solution produced orange crystals. Due to the sensitivity of the crystal to air, the crystal used for data collection was mounted in a sealed 0.3-mm Lindeman glass capillary tube.[28] Geometric and intensity data were measured with an Enraf-Nonius CAD-4 automated diffractometer equipped with graphite-monochromated

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(25) We have investigated the possible interconversion between 2 and 3 (2 ↔ 3). Treatment of complexes 2 and 3 with DMSO at reflux only yielded an identical product. Complex 3 remained unaltered when mixed with the ligand under the same conditions used to prepare complex 2. The reactions of complexes 2 and 3 with pyridine, lutidine, and phosphine bases resulted in the formation of monomeric structures. Those results will be published elsewhere. At present we cannot explain why a small difference in synthetic conditions results in the formation of a different atropisomer.

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Table VI. Crystal Analysis Parameters of Compounds 2 and 3

	compd 2	compd 3
	Crystal Data	
formula	$C_{46}H_{38}N_2O_8Pd_2\cdot C_2H_6O$	$C_{46}H_{38}N_2O_8Pd_2$
cryst size (mm)	0.18 × 0.22 × 0.20	0.19 × 0.17 × 0.23
habit	prismatic	prismatic
symmetry	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
unit cell dimens		
a, b, c (Å)	14.206 (9), 15.764 (5), 11.149 (3)	11.889 (15), 13.209 (23), 15.436 (9)
α, β, γ (deg)	92.46 (3), 95.31 (4), 116.03 (4)	87.34 (1), 78.51 (1), 87.73 (1)
packing		
V (Å^3), Z, D_c (g cm^{-3})	2224 (2), 2, 1.5002	2372 (5), 2, 1.3437
M_r, $F(000)$, μ (cm^{-1})	1005.69, 1020, 8.524	959.61, 968, 7.993
	Experimental Data	
no. of rflns		
measd	10 320	13 787
indep	9664	7501
obsd	5498	3680
range of hkl	0–18, −20 to +20, −14 to +14	0–16, −18 to +18, −21 to +21
value of R_{int}	0.018	0.019
std rflns	2 rflns every 90 min, no variation	2 rflns every 90 min, 15% intens decay
max–min transmissn factors	1.198–0.655	1.485, 0.790
	Solution and Refinement	
soln	direct methods: SIR88, DIRDIF	direct methods: SIR88, DIRDIF
refinement	least-squares on F_o with 2 blocks	least-squares on F_o with 2 blocks
H atoms	geometric calculations	geometric calculations
w scheme	$\langle w\|\Delta F\|^2\rangle$ vs $\langle F_o\rangle$ and $\langle(\sin\theta)/\lambda\rangle$	unit
final ΔF_o peaks (e Å^{-3})	1.03	1.77
R, R_w	0.075, 0.069	0.082, 0.097

Mo Kα (λ = 0.710 73 Å) radiation. All data were collected at 25 °C. Preliminary constants were determined approximately and then refined by least squares on 25 reflections. Reflections were recorded by the $\omega/2\theta$ scan technique, in the range 5° < θ < 30°. The crystal data and details of the data collection and structure analyses are summarized in Table VI. During the data collection two standard reflections were measured every 90 min. There was no evidence of crystal decomposition. The measured data were corrected for Lorentz and polarization effects, and an empirical absorption correction[29] was applied.

The structure was solved by a combination of direct methods (SIR88,[30] DIRDIF[31]) and Fourier syntheses and refined on F by full-matrix least-squares calculations. An EtOH solvate could be located. All non-hydrogen atoms were refined anisotropically, except for those in the ethanol molecule, which were refined isotropically. All H atoms were introduced at their calculated positions and included, in the least-squares refinement as fixed isotropic contributors. The final disagreement indices were R = 0.075 and R_w = 0.069. Anomalous dispersion corrections and atomic scattering factors were taken from ref 32. Calculations were performed with the XRAY80 system,[33] PARST,[34] and PESOS[35] on a VAX 11/750 computer.

Structure Determination and Refinement of Complex 3. Recrystallization by slow evaporation from a CH_2Cl_2–EtOH (99:1) solution produced some poor-quality orange crystals. The crystal was mounted in a sealed 0.3-mm Lindeman glass capillary tube and placed in the CAD-4 diffractometer, equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation, at 25 °C. Cell constants were refined by least-squares on 25 reflections. Reflections were recorded as above. The data, the details of the data collection, and structure analyses are summarized in Table VI. Two standard reflections, measured every 90 min, showed an intensity decay of 15% at the end of the process. The measured data were corrected for Lorentz and polarization effects, and an empirical absorption correction[29] was applied.

The structure was solved in a way similar to that described above. All non-hydrogen atoms were refined anisotropically (except for the C120 atom, which was in a disordered position). In the later stages of the refinement data above ($\sin\theta/\lambda$ > 0.3 Å^{-1} and unit weights were used. H atoms were treated as described in the refinement of complex 2. The final disagreement indices were R = 0.082 and R_w = 0.097. A difference Fourier map showed peaks up to 1.77 e Å^{-3}, near the palladium atoms. No better solution was found in space group $P1$. The poor quality of the crystal (various crystallizations yielded no better material) and the low number of observed reflections are the reasons for the low precision of the structure refinement.

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Supplementary Material Available: Listings of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond distances and angles for 2 and 3 (14 pages). Ordering information is given on any current masthead page.

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