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Synthesis, Structure, and Electrochemistry of Palladium Complexes with Camphor-Derived Chiral Ligands

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Direct synthesis from palladium dichloride of the camphor complexes *trans*-[PdCl$_2$(3-RC$_{10}$H$_{14}$O)$_2$] (R = NNMe$_2$, NOMe, NOH), [PdCl$_2$(3-NNMe$_2$C$_{10}$H$_{14}$O)], cis-[PdCl$_2$(3-dimethylhydrazinocamphorsulfonimide)$_2$] and [PdCl$_2$-(camphorsulfonimide−tricyclane)$_2$] has been achieved. The molecular structures obtained by X-ray diffraction analysis of *cis*-[PdCl$_2$((3-dimethylhydrazino)camphorsulfonimide)$_2$] and *trans*-[PdCl$_2$((3-dimethylhydrazino)-camphor)$_2$] show they crystallize in the orthorhombic ($P2_1P2_1P2_1$, with a = 11.515(3) Å, b = 14.504(3) Å, c = 18.546(9) Å, and Z = 4) and monoclinic ($P2_1$, a = 17.053(1) Å, b = 9.944(1) Å, c = 17.247(1) Å, β = 108.93-(1)°, and Z = 4) space groups, respectively. The redox properties of all the complexes and ligands were studied by cyclic voltammetry and, whenever convenient, controlled-potential electrolysis.

Introduction

Within our interest in the study of the coordination of chiral camphor derivatives to transition metals, we described in a previous paper[1] the preparation and characterization of several complexes derived from (1a*S*,3a*S*,7*R*)-8,8-dimethyl-7-hydroxy-1,1a,4,5,6,7-hexahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (3-hydroxycamphorsultam). The X-ray molecular structure of a square planar dimeric copper (II) complex was reported showing the double deprotonated form of the camphor ligand acting as a four electron donor in a O-bridging, N-chelating species. Camphor derivatives are important chiral auxiliaries or catalysts for stereoselective synthesis.[2−4] Having a saturated carbon skeleton, 3-hydroxycamphorsultam is a good ligand for metals in high oxidation states, providing chiral Lewis acids which catalyze effectively enantioselective Diels−Alder and similar reactions.[5,6] However, metals in low oxidation state can be applied in carbon−carbon bond formation reactions involving alkenes or alkynes. Camphor derivatives of the 1,4-diazadiene and 1-oxa-4-aza-diene type, containing double bonds, are expected to bind readily metals in low oxidation states.[7−11] Camphor-derived phosphines as ligands for palladium were already studied,[12,13] and structural analyses were performed on several complexes of 3-(hydroxymethylene)camphor and its methyl- and trifluoromethyl-substituted analogues with transition metals[14−17] and lanthanides[18] which find application as chiral NMR shift reagents, as chiral stationary phases for chromatographic enantiomer separation, or as enantioselective catalysts. Comparatively little is known about complexes of ligands containing nitrogen and oxygen donor functions. Among the characterized species, molybdenum complexes of camphorquinone monoimines and hydrazones[19,20] were reported and their optical properties investigated. The oxime of camphor coordinates through the nitrogen atom, generating a *trans* palladium complex,[21] and complexes of the four isomeric camphorquinone−dioximes were obtained with nickel,[22,23] copper, palladium, and

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platinum. The nickel and palladium complexes can act as multidentate ligands themselves, giving multinuclear frameworks with silver ions.[24]

Palladium (II) displays good coordinating ability for nitrogen ligands, and in this article we report the synthesis of some new complexes of palladium with N-coordinated chiral camphor-derived ligands. Suitable crystals for X-ray diffration analysis were obtained for two of the complexes and their structures are discussed.

The redox properties of the complexes are influenced by their electronic properties, which determine their reactivity and thus their possible applications. In order to get a further insight into the electronic characteristics of the compounds, their electrochemical behavior has been studied by cyclic voltammetry and controlled-potential electrolysis.

Results and Discussion

Synthesis of the Ligands. All ligands were derived from D-camphor ((1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), and their absolute configuration is therefore defined. The ligand labeled **L3** (isonitrosocamphor) is an ancient compound,[25,26] and is easily converted to its *O*-methyl derivative,[27-29] **L2**. Camphorquinone dimethylhydrazone (ligand **L1**) is readily obtained from camphorquinone,[30-32] Figure 1A. The ligands **L4** and **L5** are prepared from the known[33,34] 3-oxo-camphorsulfonimide ((3a*S*)-8,8-dimethyl-5,6-dihydro-3*H*-3a,6-methano-2,1-benzisothiazol-7(4*H*)-one 2,2-dioxide) as shown in Figure 1B. The structure of the two isomeric hydrazones **P1** and **P2** can be assigned by NMR on the basis of a ROESY experiment, where a strong cross-peak between the NH_2 group and the bridgehead hydrogen (at C_4) is observed in **P2**, but not in **P1**, indicating a close vicinity of the two groups in **P2**; this must therefore be the *E*-compound. Oxidation of both hydrazones **P1** and **P2** to the diazo compound **L5** is possible with elemental iodine, although this reagent in general converts hydrazones to diiodides.[35,36] Even the closely related hydrazone of camphor does not give 3-diazocamphor as product, but normal and rearranged vinylic iodides by proton elimination from intermediate iodocarbocations.[36]

Synthesis of the Complexes. Palladium dichloride reacts in dichloromethane with the camphor-type ligands **L1–L4** forming complexes with the general formula $[PdCl_2L_2]$ (**i–iv**), reaction 1.

$$PdCl_2 + 2L \rightarrow [PdCl_2L_2] \qquad (1)$$

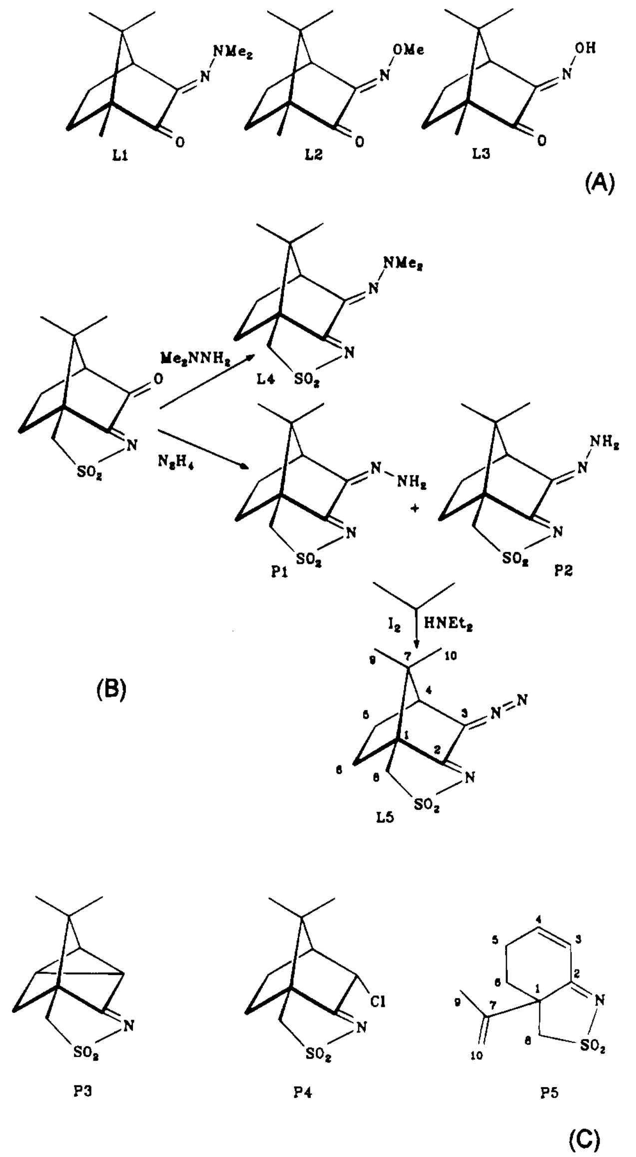

Figure 1. (A) Camphor ligands **L1–L3**. (B) Preparative scheme for **L4** and **L5** and **P1** and **P2** (isomeric forms). (C) Detected products from reaction of **L5** with acid and numbering for carbon atoms.

In contrast to the abovementioned ligands, which coordinate palladium without further reaction, the diazo group in **L5** is cleaved during the reaction and the derived organic by-products, **P3** (the tricyclane derivative), a typical product of carbene reactions of diazocamphor derivatives,[37] and *endo*-3-chlorocamphorsulfonimide **P4**,[38] have been identified, Figure 1C. The later product is also formed when **L5** is treated with aqueous HCl, which suggests that palladium dichloride reacts as a Lewis acid, leading to the formation of a species with partial cationic character and loss of dinitrogen. The cationic intermediate is then trapped by chloride to give the chorinated product. Free cations are probably not involved in the reaction since the ring-opened product **P5** is not detected. In processes where cationic intermediates occur, **P5** (at least in a minor amount) is always observed.[39,]

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Table 1. Crystallographic Data for Compounds **i** and **iv**

	i	**iv**
chem formula	$C_{24}H_{40}N_4O_2Cl_2Pd$	$C_{24}H_{38}N_6O_4Cl_2Pd$
fw	593.56	651.88
space group	$P2_1$	$P2_1P2_1P2_1$
λ(Mo Kα)/Å	0.710 69	0.710 69
ϱ_{obs}/g cm^{-3}	1.425	1.5697
μ(Mo Kα)/cm^{-1}	8.8	8.8
a/Å	17.053(1)	11.515(3)
b/Å	9.944(1)	14.504(3)
c/Å	17.247(1)	18.546(9)
β/deg	108.93(1)	90
V/Å^3	2766.5	3097.4
Z	4	4
T/°C	22	23
R^a	0.0294	0.026
$R_w{}^b$	0.0294	0.032

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.026$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[$PdCl_2$(**L1**)$_2$] (**i**)[a] and *cis*-[$PdCl_2$(**L4**)$_2$] (**iv**)

trans-[$PdCl_2$(**L1**)$_2$]			*cis*-[$PdCl_2$(**L4**)$_2$]	
Pd−Cl1	2.311(1)	[2.313(1)]	Pd−Cl1	2.281(8)
Pd−Cl2	2.292(1)	[2.308(1)]	Pd−Cl2	2.295(9)
Pd−N1	2.065(3)	[2.040(3)]	Pd−N1	2.045(3)
Pd−N3	2.052(3)	[2035(3)]	Pd−N4	2.048(2)
N1−N2	1.428(5)	[1.447(5)]	N2−N3	1.292(4)
N3−N4	1.423(5)	[1.432(5)]	N5−N6	1.305(4)
N1−C1	1.255(5)	[1.273(5)]	N1−C6	1.291(4)
N3−C11	1.279(4)	[1.268(5)]	N4−C26	1.298(4)
N2−C24	1.410(7)	[1.35(1)]	N1−S1	1.685(3)
N2−C23	1.428(7)	[1.380(9)]	N4−S2	1.696(3)
N4−C22	1.454(7)	[1.408(9)]	C6−C5	1.424(4)
N4−C21	1.462(5)	[1.440(6)]	C25−C26	1.434(4)
C1−C2	1.512(6)	[1.508(6)]	N2−C5	1.308(5)
C11−C12	1.518(6)	[1.510(5)]	N5−C25	1.304(5)
Cl2−Pd−Cl1	178.7(1)	[178.8(1)]	Cl2−Pd−Cl1	90.60(4)
N1−Pd−Cl1	90.8(1)	[90.2(1)]	N1−Pd−Cl1	90.42(8)
N1−Pd−Cl2	88.8(1)	[90.7(1)]	N4−Pd−Cl2	89.02(8)
N3−Pd−Cl1	89.8(1)	[89.6(1)]	N1−Pd−Cl2	178.94(8)
N3−Pd−Cl2	90.5(1)	[89.5(1)]	N4−Pd−Cl1	179.57(9)
C1−N1−Pd	125.1(3)	[124.8(3)]	C6−N1−Pd	126.6(2)
C11−N3−Pd	124.6(3)	[124.8(3)]	C26−N4−Pd	125.2(2)

[a] Values for the crystallographically independent second molecule are given in brackets.

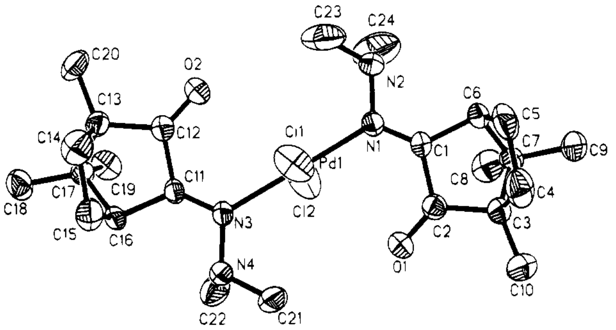

Figure 2. ORTEP drawing for *trans*-[$PdCl_2$(**L1**)$_2$] showing labeling scheme and the 50% probability ellipsoids.

The reactivity of ligand **L5**, in dichloromethane, a solvent with low coordination ability, precluded the identification of a coordination product; however using a mixture of dichloromethane/acetonitrile, [$PdCl_2$(P3)$_2$] (**vi**) was obtained. Apparently, acetonitrile stabilizes the complex and has an influence on the reactivity of **L5**. The presence of one CH_3CN molecule of crystallization *per* molecule of complex is identified by NMR and microanalysis, tables 5 and 3, respectively. A good yield (~80%) of the complex was obtained, although the organic byproducts obtained in dichloromethane do also form in minor amounts in the mixture of solvents. In contrast to the other ligands, the diazo **L5** does not remain intact upon coordination, but loses N_2 to form coordinated **P3**. At this stage the involvement of a good coordinating solvent probably accounts for the formation of complex **vi** in a good yield. In the absence of such a solvent, the metal site presents some Lewis acid character, and an incoming **L5** molecule could react in the way it normally reacts with acid, affording mainly organic products **P3** and **P4**, Figure 1C. Such side reactions, in fact occur in some extent as can be observed through the organic products identified; however, acetonitrile considerably increases the selectivity toward the formation of complex **vi**.

One of the aims of this work is to get information about the coordination ability of *N*-camphor-type ligands and the establishment of the possible geometries of derived complexes, since formally all the camphor species used by us can act as monodentate, chelating or bridging ligands. In order to create available coordination positions around palladium we did the reaction of **L1** with $PdCl_2$ in the presence of $TlBF_4$ as a chloride abstractor, and a 1:1 ligand to metal complex (**v**) was obtained; however apparently no chloride was abstracted. This ratio can point to a bidentate chelate coordination of the **L1** ligand or to a dinuclear complex. Coordination of the ligand in a bridging way, direct metal to metal interaction, or bridging through chloride are possible geometries for compound **v**. In the absence of suitable crystals for X-ray analysis further characterization was not possible.

X-ray Diffraction Analysis of *trans*-[$PdCl_2$(L1)$_2$] (i) (Structure by A.S.). Suitable crystals for X-ray diffraction analysis were obtained for complexes **i** and **iv**. The molecular crystal data are displayed in Table 1. Important bond lengths and angles are given in Table 2, and an ORTEP drawing of one of the two independent molecules of **i** is shown in Figure 2. The two independent molecules of **i** which were found in the cell unit differ particulary in the hydrazone substructure, Table 2. In complex **i**, Figure 2, palladium coordinates to the double-bonded nitrogen atom of the hydrazone groups with bond lengths within the range observed for the complex with camphoroxime (2.0−2.1 Å).[21] Although the single bonded nitrogen atom of the hydrazone group would *a priori* be expected to be more basic, it does not participate in the bonding. Coordination to palladium through nitrogen was expected, due to the high stability of the nitrogen to metal σ-bond. On the contrary, palladium is known to form weak bonds with oxygen ligands. In complex **i**, palladium displays an almost square planar coordination sphere and a *trans* arrangement of the chlorine atoms and the camphor ligands such as observed in the camphoroxime palladium complex.[21] Interestingly, the distance between palladium and the oxygen atoms of both ligands is well within the average 2.9 Å (2.951, 2.913, 2.935, 2.815 Å) for the sum of the van der Waals radii of palladium and oxygen, thus indicating some interaction, although this value is too long for a single bond. The coordination sphere could thus also be seen as a strongly distorted octahedron. This interaction must contribute to the stabilization of the observed arrangement of the camphor ligands, where the methylene bridges of the camphor skeleton are in the same half-space separated from the other by an almost planar arrangement of the N−N−Pd−N−N substructure. The values 1.208(5) Å for one molecule and 1.200(5) and 1.204(5) Å in the other are within the expected ones for the length of a C=O double bond and compare well with that in the 3-diazocamphor (1.215(8) Å)[41] species.

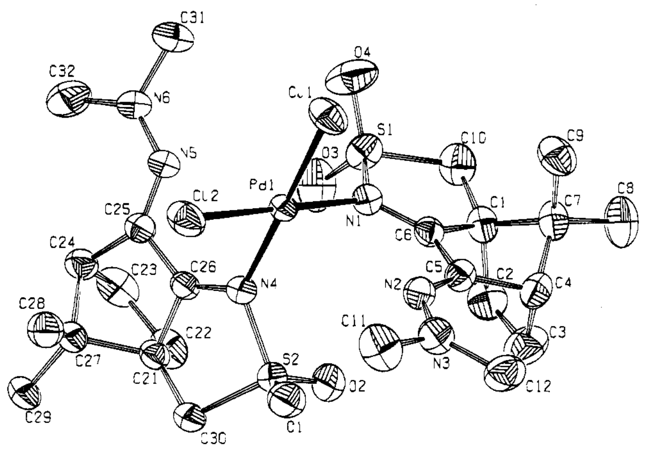

Figure 3. ORTEP drawing for *cis*-[PdCl$_2$(**L4**)$_2$] showing labeling scheme and the 50% probability ellipsoids.

The molecular structure of the free ligand **L1** is not known, but the X-ray structures of both isomers of the closely related hydrazones where the *N*-methyl groups were substituted by N–H have been studied.[30] The *E*-isomer α-camphor quinone-3-hydrazone) should resemble closely ligand **L1**. Here, a somewhat shorter C2–C3 bond (1.472(4) Å) compared to that in i (1.518(6), 1.517(6), 1.514(5), 1.512(6) Å) was found. The bond lengths in **i** correspond to a normal single bond, as observed in related camphor derivatives not containing double bonds to carbon, e.g. the camphorlactone–sulfonyloxaziridine (1.511(4) and 1.535(3) Å)[42] or the copper complex of 3-hydroxycamphorsultam (1.550(8) Å).[1] In the free hydrazone, some delocalization of the double bonds (with a resonance structure with positive charge at the terminal nitrogen and a negative charge at the C3 or at the O atom), seems to contribute to the general structure of the molecule, as the N–N bond is considerably shorter (1.332(4) Å) than in **i** (1.423(5), 1.428(5), 1.447(5) Å, respectively). In the complex, electron density is shifted toward palladium, and the contribution of the resonance structure with the charge separation becomes less pronounced.

X-ray Diffraction Analysis of *cis*-[PdCl$_2$(L4)$_2$] (iv) (Structure by W.S.). At the first sight the carbon–nitrogen double bond of a sulfonimide group resembles a carbon–oxygen double bond of a carbonyl group,[43] and in principle a similar structure could be expected for the complexes derived from **L1** and **L4** ligands. This is true insofar as a square planar coordination, with only slight deviations from 90° angles, is observed around palladium. However, in contrast to **i**, the X-ray structure of **iv**, Figure 3, revealed a *cis* arrangement of the ligands and also shows that the coordination does not occur at one of the hydrazone nitrogens but at the sulfonimide nitrogen atom, which would a priori be expected to be the weakest σ-donor nitrogen atom of the ligand. A closer look at the structure, however, gives a rationale for the unexpected behavior, at least under the point of view of the coordination atom.

Compared to those in **i** the bond lengths C6–C5 (1.424(4), 1.434(4) Å), and N2–N3 (1.292(4), 1.305(4) Å) in **iv** are considerably shorter and C5–N2 longer (1.308(5), 1.304(5) Å), which points to electron density being released from the metal toward the ligand, which upon coordination acquires a structure with extensive electron delocalization and charge separation in contrast to complex **i**. Such a delocalization can be expected to stabilize the complex. The effect of the positive charge at the terminal nitrogen atom in the corresponding resonance structure should not destabilize the metal site since it is far away from the coordination site, Figure 4. From the electronic point of view the ligand is formally acting as a π-acceptor. Although not included in the resonance structure formulated in Figure 4, there is some evidence that delocalization extends even to the sulfonyl group. Thus, the S–N bond (1.658(3) and 1.696(3) Å) is shorter than a normal single bond, as encountered in the camphorlactone–oxaziridine (1.739(3) and 1.743(2) Å).[42] It is, however, not as short as a double bond, which we have previously found in the copper complex of 3-hydroxycamphorsultam (1.579(5) Å),[1] where the shortening of the bond is induced by strong coordination to copper. This behavior is also observed in complex **iv**, although to a smaller extent. Moreover, the N–N bond length is even shorter than that in *E*-camphorquinone-3-hydrazone (1.332(4) Å),[30] suggesting that the sulfonimide is a better electron π-acceptor than the carbonyl group.

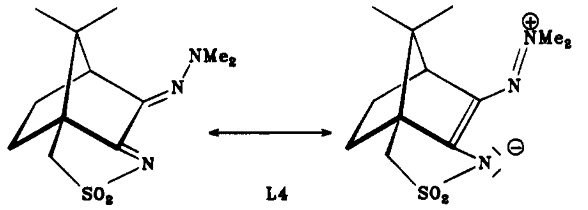

Figure 4. Resonance forms for **L4**.

IR and NMR Studies of the Complexes. Ligands **L1**, **L2**, and **L3** have similar overall structures, and therefore a similar coordination behavior would be expected. The *trans* geometry at palladium, as found by X-ray structure analysis for complex i, is also established for complexes **ii** and **iii**, on the basis of the IR data; two ν(PdCl) bands, are generally found in *cis*-complexes, while the *trans*-analogues exhibit only one.[44–46] For **v** just one ν (PdCl) band is observed, and in consequence we exclude the possibily of a *cis* geometry which could account for a chelating ligand. On the other hand, complex **vi** can be considered as having *cis* geometry, Table 3, such as found by X-ray analysis on complex **iv**.

From the X-ray diffraction analyses we conclude that coordination of **L1** and **L4** to palladium does not occur through the *a priori* expected better σ-donor atom, and therefore it is not obvious which is the atom that coordinates to the metal in the other complexes. However, comparing the IR spectra of complexes **i–iii** with those of the corresponding free ligands **L1–L3**, a general tendency of both ν_{CN} and ν_{CO} to be shifted toward higher frequencies upon coordination is observed, although less pronounced for the carbonyl group. This suggests that coordination in **ii** and **iii** occurs through the double-bonded nitrogen atom, as in complex **i**. This is also substantiated by NMR spectroscopy, since changes in the ^{13}C chemical shifts of *C*=N compared to the free ligand point to lower electron density on the carbon atom in C=N (deshielding, $\Delta\delta = 31.6$ ppm for (i), $\Delta\delta = 7.0$ ppm for (ii), and $\Delta\delta = 5.9$ ppm for (iii)), as expected for an essentially σ-donor ligand, in contrast with the effect observed on the carbonyl-carbon atom (slight shielding, $\Delta\delta = -3.5$ to -5.1 ppm). The higher σ-donating ability of the hydrazone group in **L1**, compared to the oxime function in **L2** and **L3**, is reflected in the magnitude of the deshielding of the C=N carbon upon coordination, Table 5.

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Table 3. Analytical Data for Complexes *trans*-[$PdCl_2(3\text{-}RC_{10}H_{14}O)_2$] (R = $NNMe_2$ (**i**), NOMe (**ii**), NOH (**iii**), *cis*-[$PdCl_2$(**L4**)$_2$] (**iv**), {$PdCl_2$**L1**} (**v**), and [$PdCl_2$(**P3**)$_2$] (**vi**)

		anal. found (calcd) (%)			IR (cm^{-1})[a]			
complex	color	C	N	H	ν(C=O)	ν(C=N)	ν(Pd−Cl)	% yield
i	dark orange	48.3 (48.5)	9.5 (9.5)	6.8 (6.7)	1750 s	1610 m	330 s	80
ii	yellow	46.2 (46.5)	4.6 (4.9)	6.3 (6.0)	1750 m	1630 s, br	335 s	50
iii[b]	orange	40.3 (40.4)	4.5 (4.5)	5.4 (5.1)	1745 s[c]	1665 s	340 s	40
iv	orange	40.6 (40.3)	11.4 (11.7)	5.5 (5.3)		1620 s,[d] 1500 s	328 s, 315 s	80
v	brownish	37.5 (37.4)	6.9 (7.2)	5.4 (5.1)	1745 s	1625 m, br	340 s	30
vi[e]	red-brown	38.2 (38.2)	6.0 (5.8)	4.7 (4.3)		1660 s[f]	345 m, 325 m	80

[a] In KBr pellets. [b] CH_2Cl_2 of crystallization. [c] A broad band centered at 3220 cm^{-1} is attributed to ν(OH). [d] Medium intensity bands at 3630, 3490 cm^{-1} are observed. [e] $^1/_2CH_2Cl_2$ and CH_3CN of crystallization. [f] A medium intensity band is observed at 1525 cm^{-1}.

Table 4. ^1H NMR[a] Spectral Data for the New Ligands

compd	H_3	H_4	H_5, H_6	H_8	H_9, H_{10}	others
L4[b]		3.18 (d, 4.2)	1.60 (m), 1.72 (m), 2.02 (m, 2H)	2.99 (d, 13.3), 3.18 (d, 13.3)	0.88 (s), 0.97 (s)	3.26 (s)
P1[c]		3.13 (d, 3.9)	1.40 (m), 1.52 (m), 2.00 (m), 2.13 (m)	3.14 (d, 13.7), 3.40 (d, 13.7)	0.77 (s), 0.86 (s)	8.50 (s, br)
P2[c]		2.62 (d, 3.6)	1.45 (m), 1.49 (m), 2.00 (m), 2.14 (m)	3.18 (d, 13.7), 3.40 (d, 13.7)	0.75 (s), 0.97 (s)	8.60 (s, br)
L5[b]		3.15 (d, 3.5)	1.80 (m, 2H), 2.10 (m), 2.20 (m)	3.05 (d, 13.2), 3.20 (d, 13.2)	1.05 (s), 1.07 (s)	
P3[b]	2.37 (d, 5.4)	2.10 (tr, 5.4)	2.45 (tr, 5.4) (H_5), 1.95 (m), 2.30 (m)	2.98 (d, 13.6), 3.13 (d, 13.6)	1.00 (s), 1.15 (s)	
P5[b]	6.80 (dd, 2.9; 10.0)	6.50 (dtr, 7.0; 10.0)	2.38 (m, 4H)	3.00 (d, 13.1), 3.40 (d, 13.1)	1.81 (s) (H_{10}), 4.70 (s), 5.10 (d, 1.4)	

[a] Chemical shifts δ (ppm) relative to internal TMS, multiplicity and coupling constants (Hz) in brackets; for numbering of the atoms see Figure 1, spectra obtained in a 360-MHz instrument. [b] In $CDCl_3$. [c] In DMSO-d_6.

Table 5. ^{13}C NMR Spectral[a] Data for the New Ligands and Complexes (**i**−**vi**)

compd	C_1	C_2	C_3	C_4	C_5, C_6	C_7	C_8	C_9, C_{10}
L4[b]	62.2	186.1	131.7	51.8	26.0, 28.3	48.5	49.4	18.9, 19.8
P1[c]	64.0	184.8	137.8	48.5	23.1, 29.2	45.8	47.2	19.2, 18.8
P2[c]	64.0	175.5	135.3	51.2	25.1, 27.9	47.2	49.3	18.7, 18.8
L5	64.0	183.0	60.1	50.1	26.8, 28.9	52.1	49.6	19.3, 19.4
P3	55.9	193.8	35.8	16.7	24.2 (C_5), 34.9	44.8	46.9	20.2, 20.3
P5	57.1	178.2	150.5	122.3	32.1 (C_5), 2.8	139.9	53.6	19.3, 116.7
i	58.5	201.5	175.0	53.6	23.9 (C5), 30.2	44.6	48.6	20.9, 17.7
ii	66.0	199.8	165.7	58.9	23.8, 30.1	44.9	50.8	21.0, 17.6
iii	59.9	199.5	165.4	53.0	23.6, 30.1	45.3	49.9	21.1, 17.6
iv	59.8	185.6	127.1	59.8	27.5, 25.9	51.6	50.0	20.0, 19.1
v	61.9	178.2	156.6	57.9	39.0, 33.8	50.7	53.9	31.5, 28.8
vi[d]	78.5	191.9	26.2	19.4	29.5, 51.4	51.4	51.6	20.7, 20.4

[a] In $CDCl_3$, unless stated otherwise, chemical shifts δ (ppm) relative to internal TMS; for numbering of the atoms see Figure 1, spectra obtained at 90.5 MHz. [b] Another signal is observed at 46.0 ppm. [c] In DMSO-d_6. [d] Other signals with lower intensity were observed pointing to the presence of isomers in solution; signals at $\delta = 123.9$ and 2.7 ppm are attributed to CH_3CN.

As already discussed, complex **v** was obtained from **L1** using different reaction conditions than those used in the preparation of **i**. IR and NMR data concerning compound **v** display a similar trend compared to complex **i** (e.g., in the ^{13}C NMR spectrum, $\Delta\delta_{C=N} = 32.5$ ppm upon coordination) thus suggesting a coordination through the CN double bonded nitrogen atom as authenticated by X-ray analysis for complex **i** and an overall similar trend on the electronic and bonding characteristics of the ligand. However, from analytical data a 1:1 metal to ligand ratio was observed and from the IR data we excluded the possibility of a chelating ligand since only one ν(PdCl) band is observed. If the NMR spectra of **i** and **v** are compared, similar overall characteristics are found, in contrast with that expected for a possible bridged ligand. As a consequence the geometry of complex **v** could be that of a chloride bridging dimer. However, in the absence of an X-ray molecular structure no full characterization of **v** is possible. For such complexes, isomeric forms are conceivable, and the NMR spectra do indeed show some signals of low intensity close of that of the main product, pointing to presence of isomers in solution. The exact structure of the main species in solution could, however, not be ascertained.

Several NMR ^{13}C signals indicating the presence of other isomers were also observed in complex **iii**, which is derived from *E*-isonitrosocamphor, **L3**. At this complex *E*/*Z*-isomerism of the C=N double bond is a possible explanation for the observed signals. The hydroxy function at the nitrogen shows a more pronounced tendency toward migration to the other side than does the dimethylamino or the methoxy group in ligands **L1** and **L2**, respectively, and changes in the geometry of oximes may occur upon coordination.[23] The IR pattern $\nu_{CN} = 1665$ cm^{-1}) resembles more closely the *Z*-geometry of palladium complexes of camphorquinone dioxime $\nu_{CN} = 1680$ cm^{-1} for the α-dioxime),[23] suggesting almost complete inversion of the configuration of the C=N double bond.

Ligands **L4** and **P3**, containing the sulfonimide group in the five-membered ring, are exceptions to the prefered formation of *trans*-complexes with palladium by monodentate ligands. In complex **vi** two frequencies are attributed to the Pd−Cl vibration. At these ligands, coordination has only a small effect

Table 6. ^{1}H NMR Data for Complexes *trans*-[$PdCl_2(3-RC_{10}H_{14}O)_2$] (R = $NNMe_2$ (**i**), NOMe (**ii**); NOH (**iii**)), *cis*-[$PdCl_2$(**L4**)$_2$] (**iv**), {$PdCl_2$**L1**} (**v**), and [$PdCl_2$(**P3**)$_2$] (**vi**)

complex	δ (ppm)	^{1}H[a] integration	assgnts
i	3.33 d[b]	2	CH
	3.27 s	6	CH_3
	1.5−2.1 m	8	CH_2
	1.14 s	6	CH_3
	1.00 s	6	CH_3
	0.97 s	6	CH_3
ii	5.10 s	6	CH_3
	3.31 d[c]	2	CH
	1.6−1.8 m	4	CH_2
	1.5−1.6 m	4	CH_2
	1.1 s	6	CH_3
	0.98 s	6	CH_3
	0.94 s	6	CH_3
iii[d]	12.3 s, br	*ca.* 2	OH
	4.24 d[e]	2	CH
	2.5−1.6 m	8	CH_2
	1.1 s	6	CH_3
	1.02 s	6	CH_3
	0.97 s	6	CH_3
iv	3.77 s	6	CH_3
	3.27 s	6	CH_3
	3.22 d[f]	2	CH
	3.11 d[g]	4	CH_2
	2.1−2.0 m	2	$\left.\right\}CH_2$
	1.9−1.7 m	6	
	0.93 s	6	CH_3
v[h]	3.27 s, br	1	CH
	3.13 m	6	CH_3
	1.7−2.2 m	4	CH_2
	1.23 d[i]	3	CH_3
	1.03 s	3	CH_3
	0.86 d[i]	3	CH_3
vi[j]	2.9−3.5 m	6	CH
	1.6−2.3 m	8	CH_2
	1.12 s	6	CH_3
	0.88 s	6	CH_3

[a] In $CDCl_3$ unless stated otherwise, TMS used as reference. [b] J_{HH} = 4.6 Hz. [c] J_{HH} = 4.4 Hz. [d] Other isomers are detected in ^{1}H and ^{13}C spectra. [e] J_{HH} = 4.2 Hz. [f] J_{HH} = 3.9 Hz. [g] J_{HH} = 3.5 Hz. [h] Lower intensity (*ca.* one-third of the signals are observed at δ = 200.7 and 175.4 ppm. [i] J_{HH} = 4.9 Hz. [j] Lower intensity signals attributed to the existence of other isomers in solution are observed which make difficult further assignment.

on the ^{13}C chemical shifts of the donor groups ($\Delta\delta$ = 4.0 ppm for the hydrazone, $\Delta\delta$ = 0.5 ppm for the sulfonimide on **L4** and $\Delta\delta$ = 2.6 ppm for the sulfonimide on **P3**); and the chemical shifts do not directly provide evidence for the site of coordination. However, this trend can be associated to the electronic characteristics of **L4**, which in contrast to **L1**, acts both as a σ-donor and π-acceptor, and so there is a balance between deshielding and shielding effects on the coordinating group and almost no change ($\Delta\delta$ = 0.5 ppm) on the corresponding ^{13}C shift. IR spectra, however, show a significantly changed pattern upon coordination. As the frequencies of the vibration of the C=N double bonds of hydrazone and sulfonimide groups occur at the same region in species such as camphor dimethylhydrazone (ν_{CN} = 1665 cm^{-1})[12] and camphor sulfonimide (ν_{CN} = 1660 cm^{-1}), it is not possible to assign directly the frequency values in **L4** (1665 and 1535 cm^{-1}) to the vibrations in the two distinct C=N groups. However, the shift to a lower frequency value observed for one of the C=N groups in complex **iv**, conceivably relates to the increase upon coordination of the CN distance observed in the X-ray molecular structure, Table 2, and which was interpreted on the basis of π-donation from the metal to a π*CN orbital. This suggests that such a IR band is associated with the coordinated sulfonimide group.

Table 7. Cyclic Voltammetric Data[a] for Complexes *trans*-[$PdCl_2(3-RC_{10}H_{14}O)_2$] (R = $NNMe_2$ (**i**), NOMe (**ii**), NOH (**iii**), *cis*-[$PdCl_2$(**L4**)$_2$] (**iv**), {$PdCl_2$**L1**} (**v**) and [$PdCl_2$(**P3**)$_2$] (**vi**) and Camphor-Derived Compounds

	complex		ligand		
	E_p^{ox}	E_p^{red}		E_p^{ox}	E_p^{red}
i	1.76	−1.2[b]	L1	1.48	
ii		−0.84	L2	1.86	−2.02
iii	1.81	−1.52	L3	1.53	−1.68
iv	1.52	−1.48	L4	1.54	−1.42[c]
	1.80			1.80	
v	1.70	−0.82[d]	L5	1.62	−1.20
vi		−0.84[e]	P3	1.90	−1.62

[a] Values in V ± 20 mV *vs* SCE, measured (at 200 mV s^{-1}) at a Pt electrode, in CH_2Cl_2 (unless stated otherwise)/0.2 M [NBu_4][BF_4], using as internal standard [$Fe(\eta^5-C_5H_5)_2$]$^{0/+}$ ($E_{1/2}^{ox}$ = 0.545 V). [b] In THF. [c] Reversible wave. [d] In CH_3CN. [e] A smaller intensity reduction wave is observed at E_p = −0.48 V probably due to some isomer in solution.

Electrochemical Study. The electrochemical behavior of complexes **i**−**vi** was studied by cyclic voltammetry at a platinum electrode in an aprotic medium, usually 0.2 M [NBu_4][BF_4]/CH_2Cl_2, but in some cases THF or CH_3CN were used as solvents. Controlled-potential electrolysis was performed in a few cases, either at the potential of oxidation or reduction processes, using a platinum gauze or a mercury pool as electrodes, respectively.

A preliminary account on these studies was reported.[47]

Anodic Behavior. All free ligands and complexes but complexes **ii** and **vi**, display by cyclic voltammetry oxidation waves within the range of potentials available, Table 7. The complexes display higher anodic potentials than the corresponding ligands. This trend provides an explanation for the absence of a visible oxidation process of complexes **ii** and **vi**, since the corresponding ligands (**L2** and **P3**) display anodic waves close to the oxidation limits for the system used.

As far as higher oxidation potentials can point to lower electron density on closely related systems, we consider there is an agreement between the behavior observed by cyclic voltammetry and ^{13}C NMR, since higher potentials for the anodic processes on complexes, compared to the ligands, correspond to higher deshielding on carbon. In complex **iv**, the difference on the oxidation potential of the complex and the precursor **L4** ligand is very small. This trend was expected from the ^{13}C NMR spectra, since a small shift for the sulfonimido carbon atom was observed upon coordination as a consequence of the σ-donor *versus* π-acceptor character of **L4**. Hence, we consider the anodic processes detected at the complexes occur essentially at the coordinated ligands. This electrochemical behavior suggests the HOMO of the species has an essentially ligand character.

In order to have a better insight on the redox properties of the systems we performed controlled-potential electrolysis at the potential of the first oxidation waves of ligands **L1** and **L4**, using a Pt gauze as the working electrode. This study showed that one and three electrons are involved, respectively. In **L4**, but not in **L1**, two close oxidation processes are observed by cyclic voltammetry, Table 7, also showing that the ligands have different behavior; the oxidation is probably centered at the hydrazone group on **L1**, whereas for **L4** the oxidation of the sulfonimide group can also occur.[48] In both cases the processes are accompanied by passivation of the electrodes. A parallel

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study on the corresponding complexes was essayed; however, the higher potential of the anodic processes and even more pronounced loss of sensivity of the electrodes during the electrolysis process precluded further conclusions.

Cathodic Behavior. All the reported complexes display cathodic processes, within the range −0.80 to −1.52 V, Table 7. These reduction processes occur at higher potentials than those measured for the corresponding free ligands, the exception being compound **iv**, which displays a slightly lower value consistent with the net electron effect already discussed for the ^{13}C NMR. With the exception of **iv**, the easier reduction (higher potential) of the complexes compared to the corresponding free ligands can be attributed to the electron-withdrawing ability of palladium and thus suggests a considerable influence of the metal on the LUMO of the complexes.

Controlled-potential electrolysis of complex **i** in THF, at the cathodic wave, using a Hg pool as the working electrode, shows that two electrons are involved. During the electrolysis, deposition of palladium is observed, consistent with the process having a considerable metal participation.

Controlled-potential electrolysis performed at the irreversible cathodic wave of complex **iv**, in CH_2Cl_2, corresponds to an overall multielectron process. Deposition of palladium metal is also observed during electrolysis. Cyclic voltammetry performed on the electrolyzed solution displays a reversible wave at $E_{1/2}^{red} = -1.48$ V). Under similar conditions, controlled-potential electrolysis performed at the reduction potential of the free ligand $E_p^{red} = -1.42$ V) shows that two electrons are transfered. This behavior has previously been identified for hydrazones in alkaline solutions.[40] Moreover, phenylhydrazones in acid medium show further reactivity and aniline and other amines have been identified as products in reduction processes involving four electrons *per* molecule upon controlled-potential electrolysis.[40] Therefore we could not evaluate the fate of coordinated **L4** in complex **iv** as a result of the controlled-potential electrolysis, the involvement of an overall multielectron cathodic process would be expected.

Conclusions

The ability of some camphor derived species to coordinate to palladium through imino nitrogen atoms affording square planar complexes, either displaying *trans* or *cis* geometry, is evident. In contrast with nitrogen, the oxygen atom of the ketone group of such ligands does not bind to palladium. However, some palladium−oxygen interaction has been detected through the X-ray diffraction analysis of *trans*-[$PdCl_2$(3-$NNMe_2C_{10}H_{14}O)_2$] in a *pseudo* distorted octahedral geometry.

This study shows the electronic properties of the camphor ligands are considerably versatile, and can be modified through the formal replacement of a ketone by a sulfonimide group (as in **L1** and **L4**), which results in π-acceptance of the ligand accompanied by change of the coordinated imino-N atom and of the complex geometry.

The redox properties of the complexes and ligands have been analyzed in terms of the spectroscopic characteristics of the compounds and also of the X-ray data obtained for **i** and **iv**. Evidence for the involvement of palladium in the reduction processes is obtained through palladium metal deposition upon controlled-potential electrolysis of the complexes.

Experimental Section

All manipulations and reactions involving palladium complexes were performed under dinitrogen using standard inert-gas flow and vacuum techniques. Solvents were purified before use by standard procedures. Palladium dichoride was purchased from Roth. Infrared measurements were carried out with a Perkin-Elmer 683 spectrophotometer. Mass spectra were obtained with a Varian MAT CH5 instrument (70 eV). NMR spectra were obtained on a Varian 300 and Bruker AM 360 spectrometers. The electrochemical experiments were performed on a EG&G PAR 173 potentiostat/galvanostat and a EG&G PARC 175 universal programmer. As a general procedure a 0.2 mol dm^{-3} [NBu_4][BF_4] in dichloromethane, tetrahydrofuran, or acetonitrile solution was used, either at a platinum electrode for cyclic voltammetry or a platinum gauze or a mercury pool electrodes for the controlled-potential electrolysis at oxidation and reduction processes, respectively. The values of the oxidation or reduction potentials are quoted relative to SCE, and were measured using as internal reference the redox couple [$Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ $E_{1/2}^{ox} = 0.545$ V vs SCE).

Crystallographic Data Collection and Refinement of the Structures for *trans*-[$PdCl_2(L1)_2$] (i) (Structure by A.S.). A crystal of dimensions 0.25 × 0.30 × 0.35 mm of **i** was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation $\lambda = 0.710\,69$ Å) with $\theta-2\theta$ scan mode at 22 °C. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. *Lp* correction was applied, but intensity data were not corrected for absorption effects. The structure was solved by direct methods (SHELXTL-PLUS) and completed by difference Fourier syntheses (SHELXTL-PLUS). Crystal data: $C_{24}H_{40}Cl_2O_2N_4Pd$, $M_r = 593.56$, monoclinic, $a = 17.053(1)$ Å, $b = 9.944(1)$ Å, $c = 17.247\ (1)$ Å, $\beta = 108.93(1)°$, space group $P2_1$, $Z = 4$, $D_{cal} = 1.425$ g cm^{-3}, $F(000) = 1232$, μ(Mo Kα) = 8.8 cm^{-1}. In the range $2.0° < \theta < 27°$, 12 408 independent structure factors were measured from which 11 223 were considered "observed" [$F_o \geq 4\sigma\ (F_o)$] and used for refinement. Seven hydrogen atoms could be located; the remaining H atoms were calculated and included in idealized geometry with fixed $U_{iso} = 0.05$ and 0.08 Å^2, respectively. All non-H atoms were refined with anisotropic displacement parameters. The function minimized was $[\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. The final R and R_w values were 0.029 and 0.031, respectively (inverse model: 0.035 and 0.038) (number of refined parameters: 594). Residual electron density: +0.37/−0.82 e Å^{-3}.

***cis*-[$PdCl_2(L_4)_2$] (iv) (Structure by W.S.).** The same equipment as for diffraction measurements on **i** was used. Crystal data: $C_{24}H_{38}Cl_2O_4N_6S_2Pd$, $M_r = 651.88$, orthorhombic $a = 11.515(3)$ Å, $b = 14.504(3)$ Å, $c = 18.546(9)$ Å, $V = 3097$ Å^3, measurement at 23 ± 3 °C, $\varrho_{cal} = 1.57$ g cm^{-3}, $\mu = 9.5$ cm^{-1}, $F(000) = 1512$, $Z = 4$, space group $P2_1P2_1P2_1$, (No. 19). The range of measurements was $1.0° < \theta < 25°$, with scan width $(1{:}1 + 0.25 \tan \theta)°$ (±25%). A total of 5283 independent reflections were determined of which 5063 had $I > 3\sigma(I)$. Structure determination was made with Patterson methods and difference Fourier systheses. A total of 40 heavy atoms with anisotropic thermal parameters and all hydrogen atoms were calculated in their ideal positions ($d_{C-H} = 0.96$ Å, U_{iso} 0.1 Å^2) and included in the data set but not refined. Anomalous dispersions[49] were accounted for. The function minimized was $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The final values were $R = 0.026$ and $R_w = 0.032$. The refinement of the other enantiomer was done but results in higher R-factor ($R = 0.031$, $R_w = 0.039$). The weighting scheme of Turkey and Prince[50] with three refined parameters was used ($P(1) = 1.51$, $P(2) = 0.791$, $P(3) = 0.978$). The residual electron density was +0.78 Δe/Å^{-3} (1.51 beside O5)/−1.12 Δe/Å^{-3}. All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS[51] and PLATON.[52]

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Syntheses of the Ligands. ***E*-(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2,3-dione 3-oxime (isonitrosocamphor, Ligand L3)**[25,26] **and *E*-(1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione 3-(*N*,*N*-dimethylhydrazone) (ligand L1)** were obtained as described in the literature.[30–32] The *O*-methyl ether of isonitrosocamphor (*E*-(1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione 3-(*O*-methyloxime)) has been obtained earlier by the reaction of the isonitrosocamphor with diazomethane[27,28] but is more conveniently and with high yield prepared with 10% NaOH/dimethyl sulfate, as described for the isomeric camphorquinone 2-oxime[29] (ligand **L2**).

The ligands **L4** and **L5** are derivatives of 10-camphorsulfonic acid and are obtained via 3-oxocamphorsulfonimide[33,34] ((3a*S*)-6,8-dimethyl-5,6-dihydro-3*H*-3a,6-methano-2,1-benzisothiazol-7(4*H*)-one 2,2-dioxide) as follows.

(3a*S*)-8,8-Dimethyl-5,6-dihydro-3*H*-3*a*,6-methano-2,1-benzisothiazol-7(4*H*)-one 2,2-Dioxide 7-(*N*,*N*-Dimethylhydrazone) (Ligand 4). To a solution of 3-oxocamphorsulfonimide (2.3 g, 10 mmol) in 60 mL of ethanol and 1 mL of acetic acid is added dropwise with stirring a solution of *N*,*N*-dimethylhydrazine (1.8 g, 30 mmol) in 5 mL of ethanol. After 2 h, the mixture is concentrated to 15 mL, and the precipitate is filtered off and washed several times with ether. Recrystallization from chloroform gives 2.0 g (74%) of the product, mp 215 °C, $[\alpha]_D^{22}$ = −375 (*c* = 1.0, DMSO). MS: *m/e* 269 (M$^+$), 226, 205, 69 (100%). Anal. Calcd for $C_{12}H_{19}N_3O_2S$: C, 53.5; H, 7.1; N, 15.6. Found: C, 53.2; H, 7.1; N, 15.6. For NMR data, see Tables 3 and 4.

***E*- and *Z*-(3a*S*)-8,8-Dimethyl-5,6-dihydro-3*H*-3a,6-Methano-2,1-benzisothiazol-7(4*H*)-one 2,2-Dioxide 7-Hydrazone (Compounds P1 (*Z*-Isomer) and P2 (*E*-Isomer)).** To a refluxing solution of 3-oxocamphorsulfonylimine (4.6 g, 20 mmol) in 200 mL of ethanol, acetic acid (2 mL) followed by a solution of hydrazine hydrate (3.0 g, 60 mmol) in 20 mL of ethanol are added dropwise. After cooling to room temperature, the mixture is stirred for 12 h, and concentrated in vacuum to about 40 mL. Ether (~200 mL) is added to the residue, and the precipitated *Z*-hydrazone is filtered off, washed twice with water, and dried in vacuum, to give 3.1 g (64%) of **P1** as a white powder, mp 179 °C, $[\alpha]_D^{22}$ = +178 (*c* = 1.0, DMSO). MS: *m/e* 241 (M$^+$), 198, 162, 134, 106 (100%). Anal. Calcd for $C_{10}H_{15}N_3O_2S$: C, 49.8; H, 6.3; N, 17.4. Found: C, 49.4; H, 6.2; N, 17.0. From the filtrate, the ether is removed under vacuum, and to the remaining aqueous layer is added acetone (about 5 mL). After this is allowed to stand for 3 days, the precipitated *E*-hydrazone is filtered off, washed with a small quantity of water, and dried in vacuum, to give 0.9 g (19%) of **P2** as yellow crystals, mp 151 °C, $[\alpha]_D^{22}$ = +137 (*c* = 0.5, DMSO); MS: *m/e* 241 (M$^+$), 198, 162, 106 (100%). Anal. Calcd for $C_{10}H_{15}N_3O_2S$: C, 49.8; H, 6.3; N, 17.4. Found: C 49.7; H, 6.4; N, 17.2. For NMR data, see Tables 3 and 4.

(3a*S*)-8,8-Dimethyl-7(4*H*)-diazo-5,6-dihydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-Dioxide (Ligand 5). To a mixture of *E*- or *Z*-(3a*S*-8,8-dimethyl-5,6-dihydro-3a,6-methano-2,1-benzisothiazol-7(4*H*)-one 2,2-dioxide 7-hydrazone, **P1** or **P2**, (0.38 g, 2.0 mmol) and diethylamine (0.73 g, 10 mmol) in 50 mL of THF is added dropwise a solution of I_2 (0.51 g, 2.0 mmol) in THF (10 mL). After this is stirred for 1 h, dichloromethane (20 mL) is added, the mixture is extracted twice with water, and the organic layer is dried (Na_2SO_4). After evaporation of the solvents and excess diethylamine under vacuum, the residue is recrystallized from dichloromethane/ether, leaving a yellow solid, yield 0.45 g (94%), mp 192 °C, $[\alpha]_D^{22}$ = +75 (*c* = 1.0, acetone). IR (KBr): 2100 (s), 1595 (s) cm^{-1}. MS: *m/e* 239 (M$^+$), 146, 132 (10%). Anal. Calcd for $C_{10}H_{13}N_3O_2S$: C, 50.2; H, 5.5; N, 17.6. Found: C, 50.2; H, 5.4; N 17.6. For NMR data, see Tables 3 and 4. In large scale preparations, yields are lower.

Independent Synthesis of (3a*S*,5*S*)-6,6-Dimethyl-3a,5-methano-3*H*-3a,4,4a,5,5a,5b-hexahydrocyclopropa[3,4]cyclopent[1,2-*c*]isothiazole 2,2-Dioxide P3. To a solution of 3-diazocamphorsulfonimide **L5** (2.4 g, 10 mmol), in 30 mL of dichloromethane, 10 mL of 30% aquous HCl is added dropwise. When gas evolution stops, stirring is continued for 1 h. After the addition of water (50 mL), the organic layer is extracted with saturated aqueous $NaHCO_3$ (3 × 30 mL) and dried with Na_2SO_4. After evaporation of the solvent, the residue is recrystallized from dichloromethane/ether 1:1, giving 1.4 g (*η* = 66%) of **P3**, mp 63 °C, $[\alpha]_D^{22}$ = +43 (*c* = 1, chloroform). IR (KBr): 1670 cm^{-1} (m). MS: *m/e* 211 (M$^+$), 183, 147, 132 (100%). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.8; H, 6,1; N, 6.6. Found: C, 55.9; H, 6.0; N, 6.7. For NMR data, see Tables 3 and 4.

Independent Synthesis of (3a*S*)-3a-(Methylethenyl)-4,5-dihydro-3*H*-2,1-benzisothiazole 2,2-Dioxide P5. The procedure is the same as that used for **P3**, except that 30% aqueous HF is used instead of HCl. Recrystallization from chloroform/ether yields 0.9 g (42%) of **P5**, mp 124 °C, $[\alpha]_D^{22}$ = +7.0 (*c* = 0.5, chloroform). IR (KBr): 1670 (s), 1630 (m), 1590 (s) cm^{-1}. MS: *m/e* 211 (M$^+$), 171, 147, 132 (100%). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.8; H, 6.1; N, 6.6. Found: C, 56.0; H, 6.2; N, 6.6. For NMR data, see Tables 3 and 4.

Syntheses of the Complexes. *trans*-[PdCl$_2$(3-NNMe$_2$C$_{10}$H$_{14}$O)$_2$] (i). $PdCl_2$ (0.172 g, 0.97 mmol) and 3-$NNMe_2C_{10}H_{14}O$ (0.416 g, 2.00 mmol) were stirred together in 30 cm^3 of CH_2Cl_2 for 2 days. The brown-orange suspension was then filtered to separate some unreacted $PdCl_2$ and the volume of the orange solution was reduced under vacuum to about 10 cm^3. Upon addition of 35 cm^3 Et_2O and cooling to *ca.* −5 °C, a bright orange precipitate was obtained, which was filtered off the solution and washed with Et_2O (*ca.* 0.46 g, 80% yield).

***trans*-[PdCl$_2$(3-NOMeC$_{10}$H$_{14}$O)$_2$] (ii).** A CH_2Cl_2 (50 cm^3) solution of $PdCl_2$ (0.30 g, 1.7 mmol) and 3-$NOMeC_{10}H_{14}O$ (0.66 g, 3.4 mmol) was stirred under reflux for 20 days. The unreacted $PdCl_2$ was then filtered off the solution which was then concentrated under vacuum until *ca.* 1 cm^3. Slow addition of Et_2O (1 cm^3) and cooling to −20 °C led to the precipitation of the complex. A further crop was obtained from the mother liquor upon addition of Et_2O (1 cm^3) and cooling, (*ca.* 0.48 g, 50% yield).

***trans*-[PdCl$_2$(3-NOHC$_{10}$H$_{14}$O)$_2$] (iii).** The mixture of $PdCl_2$ (0.16 g, 0.89 mmol) and 3-$NOHC_{10}H_{14}O$ (0.33 g, 1.78 mmol) was stirred in CH_2Cl_2 for 4 days and refluxed for 1 more day. Upon separation, by filtration, of unreacted $PdCl_2$ and evaporation of the solvent untill almost dryness, addition of *n*-pentane (4 cm^3) and Et_2O (1 cm^3) to the yellow solution and cooling resulted in the precipitation of the complex, which was filtered off the solution (*ca.* 0.19 g, 40% yield).

{PdCl$_2$(3-NNMe$_2$C$_{10}$H$_{14}$O)} (v). $PdCl_2$ (0.172 g, 0.97 mmol) and 3-$NNMe_2C_{10}H_{14}O$ (0.416 g, 2.00 mmol) were stirred together in 30 cm^3 of CH_2Cl_2 for 2 days. The brown-orange suspension was then filtered to separate some unreacted $PdCl_2$ and $TlBF_4$ (0.44 g, 1.5 mmol) was then added. After the suspension was refluxed for 3 days and filtration and concentration under vacuum of the dark orange solution followed by addition of Et_2O (15 cm^3) and cooling to *ca.* 5 °C, a brownish precipitate was obtained that was then filtered off and washed with Et_2O (*ca.* 0.11 g, 30% yield).

***cis*-[PdCl$_2$(L4)$_2$] (iv).** A suspension of $PdCl_2$ (0.23 g, 1.28 mmol) and **L4** (0.50 g, 1.86 mmol) in 30 cm^3 of CH_2Cl_2 was stirred for 20 h. Filtration to separate some unreacted starting material and evaporation, under vacuum, of the solvent to *ca.* 10 cm^3 afforded upon addition of 17 cm^3 of Et_2O orange needles of the complex, which was then filtered off (*ca.* 0.73 g, 80% yield).

[PdCl$_2$(P3)$_2$] (vi). $PdCl_2$ (0.085 g, 0.48 mmol) and **L5** (0.23 g, 0.96 mmol) were stirred for 12 h in a mixture of CH_3CN/CH_2Cl_2 (24:5 cm^3). Filtration and addition of 6 cm^3 of Et_2O to the solution afforded a dark red precipitate that was filtered off and washed with Et_2O, (*ca.* 0.11 g, 50% yield).

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Supplementary Material Available: Lists of anisotropic thermal parameters and hydrogen atom positions, and comprehensive tables of bond lengths and angles are included for both structures (15 pages). Ordering information is given on any current masthead page.

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