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Two orthopalladated chromophores

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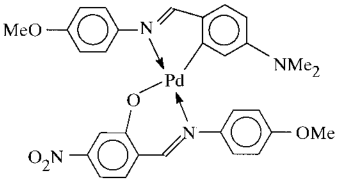
The title compounds, {5-(dimethylamino)-2-[*N*-(4-methoxyphenyl)iminomethyl]phenyl}[*N*-(4-methoxyphenyl)-4-nitrosalicylaldiminato]palladium(II), $[Pd(C_{14}H_{11}N_2O_4)(C_{16}H_{17}N_2O)]$, (I), and [4-(diethylamino)-*N*-(4-methoxyphenyl)salicylaldiminato]{2-[*N*-(4-methoxyphenyl)iminomethyl]-5-nitrophenyl}palladium(II) dichloromethane hemisolvate, $[Pd(C_{14}H_{11}N_2O_3)(C_{18}H_{21}N_2O_2)]\cdot 0.5CH_2Cl_2$, (II), both contain push–pull chromophores coordinated to Pd in a square-planar arrangement. In both compounds, the five-membered orthopalladated ring is essentially planar, while the coordinated six-membered ring is not. Deviations from a coplanar arrangement of the phenylene rings of the coordinated Schiff bases are observed in both (I) and (II) as a result of intramolecular steric interactions.

Comment

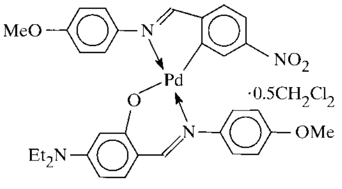
Organometallic complexes containing metallic centres bonded to organic π-electron conjugated systems are materials under investigation for applications in second-order non-linear optics (NLO). In comparison with organic compounds, they show additional chemical variables (the nature of the metal, its oxidation state, coordination geometry *etc.*) that may lead, in principle, to enhanced NLO properties. Some interesting results have been reported for organometallic fragments attached at the end of organic conjugated systems and acting as electron donor or acceptor groups (Whittall *et al.*, 1998).

A less investigated possibility is the use of metallic centres acting as conjugation bridges along push–pull systems (Buey *et al.*, 1998). In this case, conjugation should involve π interactions between the metal and the organic ligands. This obviously poses some limitations on the nature of the metal, since its coordination geometry should allow, in the optimal case, a coplanar arrangement of the metal coordination sphere and the organic conjugated ligands. Cyclometallated compounds (*e.g.* cyclometallated Schiff bases) seem a suitable choice since, in these compounds, a coplanar arrangement of metallated and *ortho*-aromatic rings must occur (Dehand & Pfeffer, 1976; Churchill *et al.*, 1980); furthermore, aromatic imines may be easily functionalized with electron donor or acceptor groups, resulting in quite highly NLO active compounds (Morley, 1995).

We have recently started a systematic investigation of the syntheses and structures of orthopalladated aromatic imines as precursors of fragments to be incorporated in polymers, and in the two complexes reported here, (I) and (II), a Pd atom is coordinated to two aromatic Schiff bases.



(I)



(II)

In both title compounds (Figs. 1 and 2), the imines are functionalized with strong electron donor–acceptor groups. In particular, one imine is of the push–pull type and contains methoxy donor and nitro acceptor groups, while the second coordinated imine is of the electron-rich type as it contains only electron-donor groups (*i.e.* methoxy and dialkylamino). The two complexes substantially differ in the nature of the cyclometallated imine which is the push–pull group in the case of (I) and the electron-rich group in the case of (II). Furthermore, in both (I) and (II), the strongest electron-donor group (*i.e.* dialkylamino) and the nitro acceptor group are placed in opposite directions with respect to the Pd atom, so as to favour a charge transfer possibly involving the metal.

Both compounds show a strong absorption band in the UV-vis region which should correspond to the HOMO–LUMO transition (the HOMO is the highest occupied molecular orbital and the LUMO is the lowest unoccupied molecular orbital). A positive solvatochromic effect is observed for this band (see *Experimental*), as generally found in second-order NLO active compounds. The effect, though rather small, is comparable with values reported in the literature for other organometallic compounds (Di Bella *et al.*, 1994). The NLO activity of the compounds has been tested by EFISH (electric field induced second harmonic) measurements in chloroform solution at λ = 1907 nm (Levine & Bethea, 1975). The values obtained, *i.e.* $\mu\beta = 120 \times 10^{-48}$ e.s.u. for (I) and $\mu\beta = 75 \times 10^{-48}$ e.s.u. for (II), indicate a moderate activity (Dalton *et al.*, 1999) (e.s.u. = electric standard unit).

The coordination around the Pd atom is substantially square planar in both complexes, showing standard values for the distances from the metal to the coordinated atoms (O'Keefe & Steel, 2000). Of the two rings to which the metal atom belongs, the cyclopalladated (five-membered) ring is substantially planar, while the salicylaldiminate (six-membered) ring is not, mainly as a result of the metal atom being out of the mean plane defined by the remaining five atoms. A trigonal planar geometry is observed around the N atom of the amino group [N1 in (I) and N3 in (II)]. The sp^2 hybridization of this atom should favour electron donation to the adjacent phenyl ring. This is consistent with the observed

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shortening of N1—C3 for (I) and N3—C19 for (II) (Allen *et al.*, 1987), and with some distortions of the bond lengths observed in the phenyl ring attached to the dialkylamino group.

Deviations from coplanarity of the phenyl rings are observed in coordinated imines of both compounds through torsions around the bonds not constrained by coordination [*i.e.* N2—C10 and N3—C21 in (I), and N4—C26 and N1—C5 in (II)]. These deviations seem to be due to internal steric repulsions [C9···C11 2.95 (1) Å and C22···C24 2.916 (9) Å for (I); C4···C8 2.871 (9) Å and C25···C27 2.902 (9) Å for (II)], and also to short contacts involving atoms of different ligands [C8···C20 3.44 (1) Å, C8···C21 3.237 (9) Å and O3···C15 2.929 (9) Å for (I); C13···C26 3.12 (1) Å and C13···C31 3.44 (1) Å for (II)]. These contacts, in particular those involving atoms of different ligands, probably also play a role in determining the non-planar conformation of the six-membered ring containing the Pd atom.

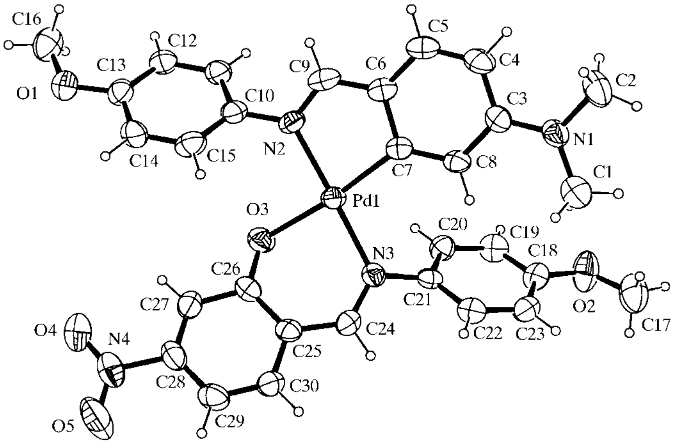

Figure 1

The molecule of (I) with displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

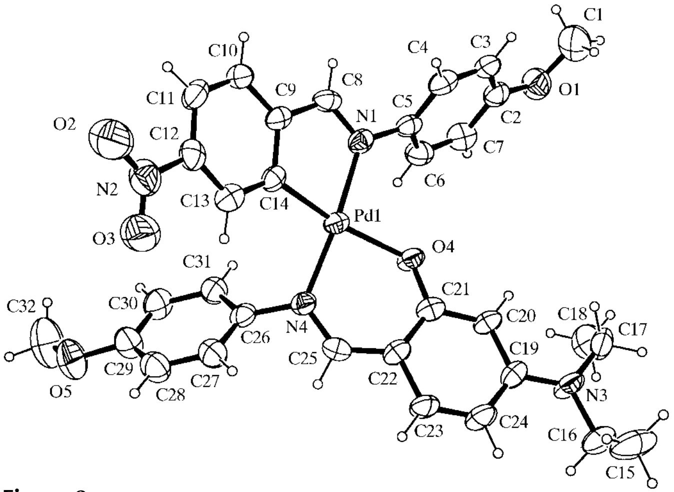

Figure 2

The molecule of (II) with displacement ellipsoids at the 50% probability level. The solvent molecule is not shown. H atoms are shown as small spheres of arbitrary radii.

In the case of (II), solvent molecules (dichloromethane) in special positions (binary axis) are also present in the crystals. Although the C and Cl atoms of the solvent molecule have highly anisotropic displacement parameters, no evidence of static disorder was found.

Experimental

Compound (I) was prepared by reaction of di-μ-acetato-bis({5-(dimethylamino)-2-[*N*-(4-methoxyphenyl)iminomethyl]phenyl}palladium(II)) with *N*-(4-methoxyphenyl)-4-nitrosalicylaldimine and compound (II) was prepared by reaction of di-μ-acetato-bis({2-[*N*-(4-methoxyphenyliminomethyl)-5-nitrophenyl}palladium(II)) with *N*-(4-methoxyphenyl)-4-(diethylamino)salicylaldimine. In both cases, a molar ratio of 2:1 of the imine to the dinuclear complex was used. Reactions were performed at room temperature for 1 h in CH_2Cl_2/ethanol solution. Melting points: 568 K (decomposition) for (I) and 584 K (decomposition) for (II). Analysis for (I): Pd 16.9% calculated, 16.6% found; for (II): Pd 16.1% calculated, 15.9% found. UV-vis λ_{max}/nm: 421 in ethyl acetate (μ = 1.78 D) and 425 in dimethylformamide (DMF) (μ = 3.82 D) for (I); 358 in ethyl acetate and 362 in DMF for (II). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation from chloroform for (I) and from dichloromethane–hexane for (II).

Compound (I)

Crystal data

$[Pd(C_{14}H_{11}N_2O_4)(C_{16}H_{17}N_2O)]$
M_r = 630.96
Orthorhombic, $Pca2_1$
a = 24.41 (2) Å
b = 14.479 (6) Å
c = 7.630 (4) Å
V = 2697 (3) Å^3
Z = 4
D_x = 1.554 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 8.2–9.5°
μ = 0.74 mm^{-1}
T = 293 (2) K
Prism, orange
0.50 × 0.10 × 0.04 mm

Table 1

Selected geometric parameters (Å, °) for (I).

Pd1—C7	2.014 (6)	C3—C8	1.400 (8)
Pd1—N2	2.037 (5)	C4—C5	1.348 (9)
Pd1—N3	2.055 (5)	C5—C6	1.393 (9)
Pd1—O3	2.062 (4)	C6—C7	1.424 (8)
N1—C3	1.366 (8)	C7—C8	1.392 (8)
C3—C4	1.396 (9)		
C7—Pd1—N2	81.3 (2)	C10—N2—Pd1	127.3 (4)
C7—Pd1—N3	100.3 (2)	C21—N3—Pd1	121.9 (4)
N2—Pd1—N3	177.8 (2)	C26—O3—Pd1	120.5 (4)
C7—Pd1—O3	173.0 (2)	C8—C7—C6	117.0 (6)
N2—Pd1—O3	92.2 (2)	C8—C7—Pd1	131.8 (4)
N3—Pd1—O3	86.2 (2)	C6—C7—Pd1	111.1 (5)
C20—C21—N3—C24	133.4 (6)	C24—C25—C26—O3	−9.6 (13)
C21—N3—C24—C25	−171.5 (6)	C25—C26—O3—Pd1	−31.7 (13)
N3—C24—C25—C30	−166.9 (7)	C26—O3—Pd1—N2	−135.2 (7)
C5—C6—C9—N2	−176.7 (7)	O3—Pd1—N2—C9	−179.8 (5)
C6—C9—N2—C10	178.5 (6)	Pd1—N2—C9—C6	−2.8 (8)
C9—N2—C10—C15	−131.3 (7)	N2—C9—C6—C7	0.7 (9)
N3—C24—C25—C26	22.1 (10)		

Data collection

Enraf–Nonius MACH3 diffractometer
ω/θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.939$, $T_{\max} = 1.000$
8378 measured reflections
8378 independent reflections
4353 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.054$
$\theta_{\max} = 30.0°$
$h = -34 \rightarrow 34$
$k = -20 \rightarrow 20$
$l = -10 \rightarrow 10$
2 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0565$
$wR(F^2) = 0.124$
$S = 0.96$
7823 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.11 (5)

Compound (II)

Crystal data

$[\mathrm{Pd(C_{14}H_{11}N_2O_3)(C_{18}H_{21}N_2O_2)]\cdot 0.5CH_2Cl_2}$
$M_r = 701.48$
Monoclinic, $C2/c$
$a = 31.582$ (10) Å
$b = 7.5847$ (10) Å
$c = 26.557$ (6) Å
$\beta = 104.96$ (3)°
$V = 6146$ (3) Å^3
$Z = 8$

$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 8.4$–$11.8°$
$\mu = 0.74$ mm^{-1}
$T = 293$ (2) K
Prism, dark orange
0.50 × 0.10 × 0.06 mm

Data collection

Enraf–Nonius MACH3 diffractometer
ω/θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.952$, $T_{\max} = 1.000$
7552 measured reflections
7388 independent reflections
3705 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.060$
$\theta_{\max} = 28.0°$
$h = -41 \rightarrow 40$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 34$
1 standard reflection
frequency: 120 min
intensity decay: 1%

Table 2
Selected geometric parameters (Å, °) for (II).

Pd1—C14	1.984 (6)	C19—C24	1.416 (9)
Pd1—N4	2.018 (5)	C20—C21	1.407 (8)
Pd1—N1	2.049 (5)	C21—C22	1.414 (8)
Pd1—O4	2.073 (4)	C22—C23	1.421 (8)
N3—C19	1.362 (8)	C23—C24	1.349 (9)
C19—C20	1.392 (8)		
C14—Pd1—N4	96.9 (2)	C5—N1—Pd1	127.4 (4)
C14—Pd1—N1	80.6 (2)	C26—N4—Pd1	122.7 (4)
N4—Pd1—N1	173.1 (2)	C21—O4—Pd1	123.3 (4)
C14—Pd1—O4	168.2 (2)	C13—C14—Pd1	129.9 (5)
N4—Pd1—O4	89.70 (18)	C9—C14—Pd1	112.7 (4)
N1—Pd1—O4	93.91 (18)		
C23—C22—C25—N4	172.1 (6)	O4—C21—C22—C25	8.5 (9)
C22—C25—N4—C26	168.5 (6)	C21—C22—C25—N4	−16.6 (10)
C25—N4—C26—C31	−130.0 (6)	C22—C25—N4—Pd1	−6.2 (9)
C6—C5—N1—C8	−131.0 (6)	N1—C8—C9—C14	−3.3 (8)
C5—N1—C8—C9	−177.0 (5)	C8—C9—C14—Pd1	0.4 (7)
N1—C8—C9—C10	172.9 (6)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.151$
$S = 0.98$
7388 reflections
393 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}

All H atoms were positioned stereochemically and refined as riding, with $U_{\rm iso}$ equal to $U_{\rm eq}$ of the carrier atom, and C—H distances in the range 0.93–0.97 Å. For (I), symmetry-equivalent reflections were not merged. The total of 8378 reflections includes 3634 Friedel pairs. The Flack (1983) parameter was refined with *TWIN* and *BASF* instructions (and *MERG* 0) according to the *SHELXL*97 (Sheldrick, 1997) manual.

For both compounds, data collection: *MACH*3 *Software* (Nonius, 1996); cell refinement: *CELDIM* (Nonius, 1996); data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1166). Services for accessing these data are described at the back of the journal. H atoms are shown as small spheres of arbitrary radii.

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