Bis(μ-trifluoroacetato-O,O')bis{[3-chloro-6-methyl-2-(N-methyl-N-nitrosoamino)-phenyl-C,N^{N=O}]palladium(II)}

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Abstract

The title compound, [Pd$_2$(C$_8$H$_8$N$_2$ClO)$_2$(C$_2$F$_3$O$_2$)$_2$], contains a palladium(II) centre with pseudo square-planar coordination and a strong interaction with the N-donor atom, which results in a Pd—N distance of 1.938 (7) Å. The two coordination planes of the dinu-clear complex are parallel and form a boat structure.

Comment

The *ortho*-H atom of differently substituted *meta*-toluidine derivatives and some of their analogues can be activated by cyclopalladation (Mossi, Klaus & Rys, 1992). In all of the cases studied, the position *para* to the toluidinic methyl group was *ortho*-palladated. The sterically more demanding centre between this methyl group and the amino function became accessible for cyclo-metallation by Pd^{II} only when the corresponding *N*-nitroso toluidine 2-chloro-5,*N*-dimethyl-*N*-nitrosoaniline was reacted with palladium(II) acetate in the presence of trifluoroacetic acid. This reaction afforded dark red crystals of the title compound, (1).

(I)
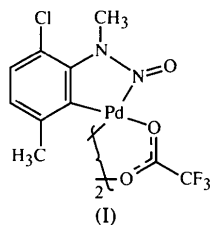
This is the first X-ray structure analysis of a cyclo-palladated *N*-nitrosoaniline with a phenyl moiety bear-ing substituents, whereas analogous Pd^{II} complexes with unsubstituted *N*-nitrosoanilines have been described before (Constable, McDonald & Shaw, 1980; Albinati, Affolter & Pregosin, 1990). The crystal structure analy-sis of (1), with the Pd—C bond at the position between

the methyl and the amino group, reveals some new as-pects of the topological arrangement around the metal centre, in a complex with significant steric hindrance exerted by the neighbouring methyl substituent.
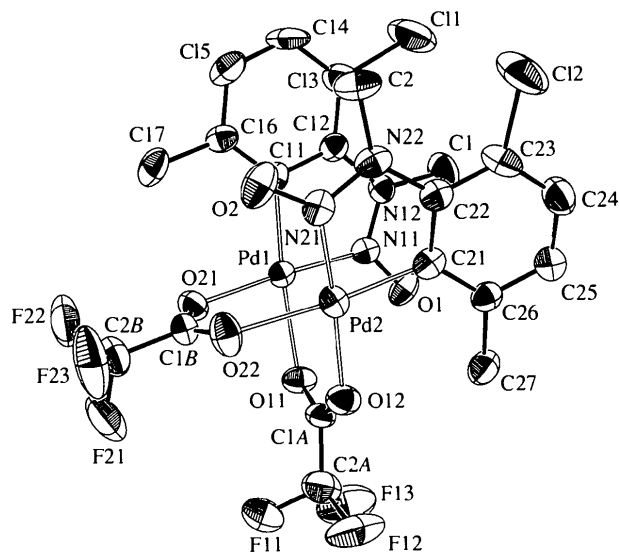

Fig. 1. Molecular structure of (1) showing 50% probability displace-ment ellipsoids. H atoms are omitted for clarity.

Complex (1) crystallizes as a dinuclear species with the two cyclopalladated units bridged by trifluoroacetate groups. Since the bond distances and angles of the two 'halves' of the molecule do not differ significantly, the relevant structural discussion will be restricted to a single Pd-centred environment. The Pd^{II} centre is coordinated, with slightly distorted square-planar ge-ometry, to the nitroso N atom (N11), the phenylic *ortho*-C atom (C11) and to both non-equivalent tri-fluoroacetato groups (O11/O21), which form bridges to the other Pd^{II} (Fig. 1). The slight deviation from a square-planar arrangement around Pd is demon-strated by the angles of 176.4 (3)° for N11—Pd1—O21 and 174.4 (3)° for C11—Pd1—O11. The angle of about the C,N-coordinated Pd^{II} atom within the five-membered metallacycle amounts to only 80.8 (3)°, which is obviously the result of the Pd—N [1.938 (7) Å] and the Pd—C [1.983 (5) Å] distances being signifi-cantly longer than the remaining C—C (1.39 Å), C—N [1.406 (9) Å] and N—N [1.328 (11) Å] bonds of the five-membered ring. The large Pd···Pd distances of 2.8901 (13) (intramolecular) and 3.367 (2) Å (inter-molecular) exclude any interaction between the Pd cen-tres. The two coordination planes containing the biden-tate *N*-nitrosotoluidino ligands are parallel, resembling the walls of a boat whose base consists of the bent trifluoroacetato bridges. The boat structure is quite common for dinuclear complexes (Fuchita, Hiraki & Uchiyama, 1983; Selbin, Abboud, Watkins, Gutierrez

& Fronczek, 1983; Alonso, Juanes, de Mendoza & Rodriguez-Ubis, 1992). The bond distance Pd1—Cl1 of 1.983 (5) Å is in agreement with known values. The fact that the Pd—O11 distance [2.192 (8) Å] *trans* to the C-atom donor C11 is longer than the Pd—O21 distance [2.054 (7) Å] *trans* to the nitroso N-atom donor N11, reflects the larger *trans* influence (Pidcock, Richards & Venanzi, 1966; Appleton, Clark & Manzer, 1973; Huheey, Keiter & Keiter, 1993) of the former.

The relatively strong coordinative interaction between the metal centre and the N-donor atom is illustrated by the Pd1—N11 bond distance of 1.938 (7) Å. This value seems to lie within the range of normal covalent metal–nitrogen bond distances. Unfortunately, complexes analogous to the title compound containing trifluoroacetato ligands *trans* to a Pd—N bond have not yet been found in the literature. The formation of a comparably short Pd—N bond in complex (1) seems to be crucial for the formation of the metallacycle in spite of the steric pressure exerted by the *meta* methyl substituent. Thus, the trifluoroacetic acid added to the reaction mixture not only enhances the reactivity of the palladium(II) species employed (Mossi, Klaus & Rys, 1992), but also acts as a bridging ligand with a weak *trans* influence necessary for the formation of a short Pd—N bond.

From the N—N bond distance of 1.328 (11) Å and the N—O bond length of 1.242 (9) Å it can be deduced that the palladium(II)-coordinated *N*-nitroso moiety within the crystal is the resonance hybrid of both possible electronic structures (N—N=O *versus* $^+$N=N—O$^-$) (Looney, Phillips & Reilly, 1957; D'Agostino & Jaffé, 1970) as the standard values are 1.450 Å for the N—N single bond and 1.250 Å for the N=N double bond (Huheey, 1983), as well as 1.210 Å for the N=O double bond (Huheey, 1983). The formation of a five-membered palladacycle in complex (1) reduces the bond angle between C11, C12 and the toluidinic N atom N12 to 116.1 (6)°, compared with a theoretical angle of 120.0° in the free cyclometalland.

Experimental

Complex (1) was synthesized by reaction of palladium(II) acetate (0.050 g, 0.272 mmol) with 2-chloro-5,*N*-dimethyl-*N*-nitrosoaniline (0.056 g, 0.25 mmol) and trifluoroacetic acid (0.4 ml, 5.4 mmol) in 3 ml of dioxane for 4 h at 338 K. Recrystallization from benzene afforded dark red crystals of (1). ^{1}H NMR [(D$_6$)acetone, 300 MHz]: 2.29 (s, CH$_3$), 3.48 [s, N(NO)CH$_3$], 6.86 [d, J = 8.0, H—C(4)], 7.23 p.p.m. [d, J = 8.0, H—C(5)]. ^{13}C NMR [(D$_6$)DMSO, 125 MHz]: 23.5 (CH$_3$), 36.2 [N(NO)CH$_3$] 125.1, 126.8, 129.9, 140.8, 140.8 [C(2), C(3), C(4), C(5), C(6)], 142.7 [C(1)—Pd], 159.0 p.p.m. (q, CF$_3$COO$^-$). ^{19}F NMR [(D$_6$)acetone, 300 MHz]: −74.42 p.p.m. (CF$_3$). Analysis: calculated for C$_{10}$H$_8$ClF$_3$N$_2$O$_3$Pd (M_r = 403.0) C 29.80, H 2.00, N 6.95, O 11.91, Pd 26.40%; found C 29.89, H 2.02, N 6.78, O 12.01, Pd 24.54 ± 0.25%.

Crystal data

[Pd$_2$(C$_8$H$_8$N$_2$ClO)$_2$-
(C$_2$F$_3$O$_2$)$_2$]
M_r = 806.07
Monoclinic
$P2_1/c$
a = 17.194 (8) Å
b = 12.293 (4) Å
c = 18.938 (9) Å
β = 138.54 (3)°
V = 2650.4 (20) Å^3
Z = 4
D_x = 2.02 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3 still
  exposures on scanner
θ = 4–26°
μ = 1.645 mm^{-1}
T = 298 (2) K
Plate
0.20 × 0.15 × 0.08 mm
Dark red

Data collection

Scanner Stoe IPDS diffrac-
  tometer
Oscillation scans
Absorption correction:
  none
9933 measured reflections
4692 independent reflections
3100 observed reflections
  [$I > 2\sigma(I)$]

R_{int} = 0.0584
θ_{max} = 26°
h = −20 → 21
k = −15 → 13
l = −21 → 23
No standard reflections

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0593
$wR[F^2 > 2\sigma(F^2)]$ = 0.1191
S = 1.129
3100 reflections
337 parameters
H atoms placed in calculated
  positions
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 11.0225P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.001
$\Delta\rho_{max}$ = 0.501 e Å^{-3}
$\Delta\rho_{min}$ = −0.622 e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables
  for Crystallography* (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd1	0.47859 (7)	0.21501 (5)	0.26136 (6)	0.0495 (2)
Pd2	0.49164 (7)	−0.01878 (5)	0.25615 (7)	0.0562 (2)
O11	0.3509 (7)	0.1896 (5)	0.0894 (6)	0.065 (2)
O12	0.3738 (7)	0.0091 (6)	0.0955 (7)	0.074 (2)
O21	0.3352 (6)	0.1812 (6)	0.2258 (6)	0.067 (2)
O22	0.3347 (7)	−0.0008 (6)	0.2131 (8)	0.084 (3)
N11	0.6103 (7)	0.2402 (5)	0.2883 (7)	0.050 (2)
O1	0.6022 (7)	0.2474 (5)	0.2175 (6)	0.069 (2)
N12	0.7165 (7)	0.2462 (6)	0.3893 (7)	0.054 (2)
C1	0.8164 (12)	0.2634 (13)	0.4098 (13)	0.109 (5)
C14	0.8061 (6)	0.2316 (7)	0.6389 (4)	0.099 (4)
C15	0.6960 (7)	0.2256 (6)	0.5954 (5)	0.090 (4)
C16	0.5955 (5)	0.2245 (5)	0.4853 (6)	0.059 (2)
C11	0.6052 (5)	0.2295 (5)	0.4188 (4)	0.053 (2)
C12	0.7153 (6)	0.2355 (5)	0.4624 (5)	0.056 (2)
C13	0.8158 (4)	0.2365 (7)	0.5724 (6)	0.086 (4)
C17	0.4795 (12)	0.2146 (10)	0.4463 (11)	0.086 (4)
Cl1	0.9586 (4)	0.2329 (7)	0.6376 (4)	0.189 (3)
N21	0.5930 (9)	−0.0480 (6)	0.4053 (9)	0.064 (2)
O2	0.5587 (9)	−0.0476 (7)	0.4435 (8)	0.097 (3)
N22	0.7077 (9)	−0.0620 (6)	0.4714 (8)	0.066 (2)
C2	0.7839 (15)	−0.0664 (13)	0.5853 (12)	0.107 (5)

C24	0.8664 (5)	−0.0793 (7)	0.4081 (6)	0.088 (4)
C25	0.7752 (7)	−0.0533 (6)	0.3002 (6)	0.079 (3)
C26	0.6636 (6)	−0.0323 (5)	0.2509 (4)	0.058 (3)
C21	0.6433 (5)	−0.0373 (5)	0.3094 (5)	0.058 (3)
C22	0.7345 (6)	−0.0632 (5)	0.4172 (5)	0.059 (3)
C23	0.8461 (5)	−0.0842 (6)	0.4666 (4)	0.079 (3)
C27	0.5708 (12)	−0.0023 (10)	0.1329 (10)	0.080 (3)
Cl2	0.9670 (4)	−0.1252 (5)	0.5985 (4)	0.149 (2)
Cl*A*	0.3271 (8)	0.1006 (9)	0.0501 (8)	0.057 (2)
C2*A*	0.2308 (7)	0.0955 (7)	−0.0655 (7)	0.097 (4)
F11	0.1268 (8)	0.1173 (15)	−0.1089 (9)	0.216 (7)
F12	0.2131 (11)	0.0046 (8)	−0.1131 (9)	0.158 (4)
F13	0.2306 (14)	0.1651 (10)	−0.1187 (10)	0.172 (5)
Cl*B*	0.2963 (9)	0.0876 (10)	0.2075 (9)	0.065 (3)
C2*B*	0.1855 (9)	0.0841 (7)	0.1730 (8)	0.093 (4)
F21	0.0928 (7)	0.1099 (14)	0.0716 (9)	0.198 (6)
F22	0.1776 (9)	0.1544 (9)	0.2201 (10)	0.155 (5)
F23	0.1616 (10)	−0.0099 (7)	0.1870 (12)	0.181 (6)

Table 2. *Selected geometric parameters* (Å, °)

Pd1—N11	1.938 (7)	Pd1···Pd2	2.8901 (13)
Pd1—C11	1.983 (5)	N11—O1	1.242 (9)
Pd1—O21	2.054 (7)	N11—N12	1.328 (11)
Pd1—O11	2.192 (8)	N12—C12	1.406 (9)
N11—Pd1—C11	80.8 (3)	O21—Pd1—O11	82.2 (3)
N11—Pd1—O21	176.4 (3)	C11—C16—C17	124.4 (7)
C11—Pd1—O21	101.9 (3)	C11—C12—N12	116.1 (6)
N11—Pd1—O11	94.9 (3)	C12—C13—Cl1	125.0 (5)
C11—Pd1—O11	174.4 (3)		

All H atoms were placed in calculated positions with fixed isotropic displacement parameters (U_{iso} = 0.080 Å²). Some slightly disordered parts of the compound were refined with constraints or restraints. The C atoms in the phenyl rings were fitted to a regular hexagon with d = 1.39 Å. The C—F distance was restrained to 1.320 (1) Å. Some of the standard deviations are larger due to some libration of terminal groups, which is observed quite frequently with organometallic compounds.

Data collection: *EXPOSE* (Stoe & Cie, 1993). Cell refinement: *CELL* (Stoe & Cie, 1993). Data reduction: *CONVERT* (Stoe & Cie, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976; Larson *et al.*, 1986). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1,3-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-7-yl)(dimethylphenylphosphine)-gold(I)

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Abstract

In [Au(PMe₂Ph)T], where T is the theophyllinate ligand, $C_7H_7N_4O_2^-$ (theophylline = 3,7-dihydro-1,3-dimethyl-1H-purine-2,6-dione), the Au atom is linearly coordinated by the P atom of the dimethylphenylphosphine ligand and the deprotonated N atom at position 7 of the theophyllinate ligand. Bond parameters involving Au are: Au—N 2.071 (9), Au—P 2.233 (3) Å and N—Au—P 177.5 (2)°.

Comment

Tertiary phosphines, PR_3, are the preferred ligands in the coordination chemistry of gold. In fact, much of the progress in gold chemistry in recent years has de-