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Hybrid Ligands. Structure of a Palladium(II) Complex Containing a Pyrazolol-Derived Phosphine Ligand, $[(o\text{-}\mathrm{C_6H_4CH_2NMe_2})\mathrm{Pd}(\mathrm{Ph_2P}\{\overline{\mathrm{C{=}C(O)N(Ph)N{=}C}}\mathrm{(Me)}\})]$

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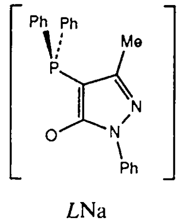
Abstract

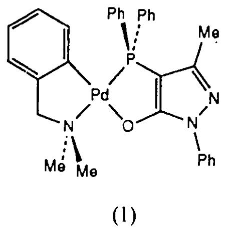
In the title compound, {2-[(dimethylamino-κN)methyl]phenyl-κC}(4-diphenylphosphino-κP-3-methyl-1-phenyl-5-pyrazololato-κO)palladium(II) 0.5-benzene solvate, $[\mathrm{Pd}(\mathrm{C_{22}H_{18}N_2OP})(\mathrm{C_9H_{12}N})].0.5\mathrm{C_6H_6}$, the Pd atom, which is in a quasi-planar environment, is complexed by two chelating three-electron-donor ligands, with P and N atoms occupying *trans* positions. The plane defined by the aromatic pyrazole ring is coplanar with the metal plane. The angle between the N-bonded phenyl ring and the metal plane is 8°.

Comment

Chelating *P*,*O*-ligands have demonstrated an extremely rich coordination chemistry, the most striking examples being some β-keto and β-ether phosphines which have been used successfully in catalytic processes of industrial relevance (Bader & Lindner, 1991; Keim, Behr, Gruber, Hoffmann, Kowaldt, Kürschner, Limbäcker & Sistig, 1986; Dupont, Gomes Carneiro, Luke & Matt, 1988; Knowles, Sabacky & Vineyard, 1974). In a number of catalytic reactions such unsymmetrical ligands induce high selectivities which cannot be achieved with symmetrical chelates (Behr, Freudenberg & Keim, 1986). It is also well established that phosphines which contain functional substituents based on oxygen-donor atoms may often efficiently enhance the reactivity of transition-metal complexes, in particular when the functional ligand is acting as a semi-labile ligand (Werner, Stark, Schulz & Wolf, 1992) or when the functional group is capable of selective binding to the substrates which will be transformed in the coordination sphere (Powell, Kuksis, May, Nyberg & Smith, 1981). As a part of our studies on hybrid ligands, we recently developed a synthesis of the pyrazolone-derived phosphine salt *L*Na, which is suitable for the formation of *P*,*O*-chelate complexes (Matt, Sutter-Beydoun, Brunette, Balegroune & Grandjean, 1993). The main features of pyrazole moieties are their high stability in acidic and neutral media as well as their strong electron-withdrawing character, which is superior to the $\mathrm{CF_3}$ group in strength (Stary & Freiser, 1975). This latter property may, in principle, affect the coordination behaviour of donor atoms connected to the pyrazole ring and allow the synthesis of electron-poor *P*,*O*-chelate systems. In this paper we present the synthesis and structure of the palladium(II) complex (1), containing two chelating ligands: the pyrazololato ligand L^- and an anion derived from dimethylbenzylamine.



*L*Na



(1)

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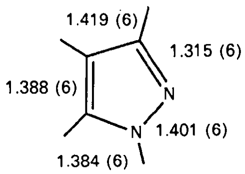
A perspective view of the molecule with atom labelling is shown in Fig. 1. The Pd atom is in a quasi-planar environment and is complexed by two chelating three-electron-donor systems. The bite angles of these chelates [82.6 (1)° for the *N,C* ligand and 86.76 (9)° for the phosphine ligand] are close to those found in a number of other five-membered *N,C* and *P,O* metallocycles (Braunstein, Matt, Nobel, Bouaoud & Grandjean, 1986). The N1—Pd—O angle is about 8° smaller than the P—Pd—C11 angle. This situation is likely to reflect some bonding interaction between the O atom and an *N*-methyl group rather than steric interactions between the PPh_2 group and the metallated aryl ring, the plane of which practically bisects the two P—Ph bonds. The pyrazole ring is planar and the distances within this ring are consistent with its aromaticity (O'Connell, Ramsay & Steel, 1985):



The pyrazole plane and the metal plane are coplanar within experimental error. The small dihedral angle of 8 (1)° between the pyrazole plane and that of the C5 phenyl group illustrates the high conjugation between these rings. In contrast to the P- and O-containing ring which is nearly planar (maximum deviation 0.025 Å for Cl), the *N,C* palladocycle is puckered in order to accommodate the sp^3 hybridization of the CH_2 carbon atom. It has a geometry characterized by the CH_2 and the C16 carbon atoms lying 0.75 and 0.43 Å, respectively, above the metal plane. The P—C1 bond length [1.762 (5) Å] is significantly shorter than the two other P—C bond lengths [1.823 (5) and 1.833 (5) Å]. This is consistent with some electron delocalization within the anionic P- and O-containing ligand. The Pd—P and Pd—O bond lengths lie in the expected range (Matt, Ingold, Balegroune & Grandjean, 1990).

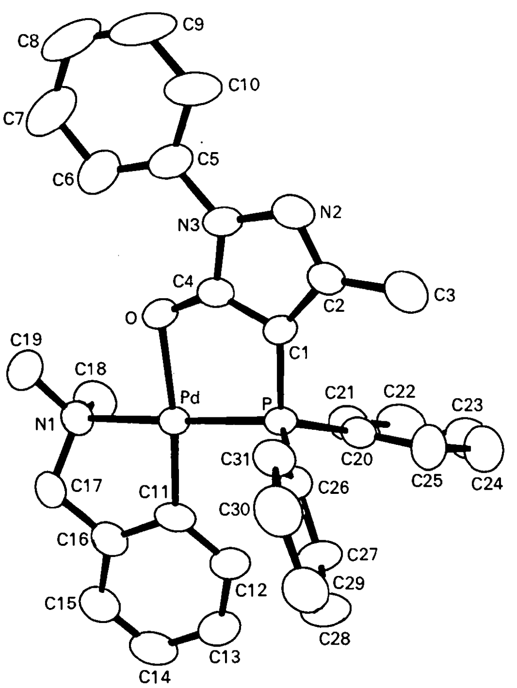


Fig. 1. Molecular configuration and atom-labelling scheme for the title compound. Probability ellipsoids are displayed at 50% and H atoms are omitted.

Experimental

Crystal data

[Pd($C_{22}H_{18}N_2OP$)($C_9H_{12}N$)]-0.5C_6H_6
M_r = 637.03
Monoclinic
$P2_1/n$
a = 12.148 (12) Å
b = 18.360 (7) Å
c = 14.815 (4) Å
β = 112.39 (4)°
V = 3055 (2) Å^3
Z = 4
D_x = 1.385 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9-12°
μ = 0.679 mm^{-1}
T = 294 K
Prism
0.18 × 0.16 × 0.12 mm
Yellow
Crystal source: benzene/dichloromethane/pentane

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5843 measured reflections
3310 independent reflections
3310 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 21$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity variation: 1.4%

Refinement

Refinement on F
R = 0.033
wR = 0.053
S = 1.16
3310 reflections
361 parameters
H-atom parameters not refined

$w = [\sigma^2(I) + (0.04F^2)^2]^{-1/2}$
$(\Delta/\sigma)_{\rm max}$ = 0.3
$\Delta\rho_{\rm max}$ = 0.60 e Å^{-3}
$\Delta\rho_{\rm min}$ = 0.05 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
Pd	0.85960 (3)	0.11360 (2)	0.39395 (2)	2.609 (6)
P	0.7200 (1)	0.08044 (7)	0.24905 (8)	2.75 (2)
O	0.9331 (3)	0.1806 (2)	0.3127 (2)	3.36 (7)

N1	0.9957 (4)	0.1461 (2)	0.5287 (3)	3.29 (9)
N2	0.8118 (4)	0.1936 (2)	0.0559 (3)	3.58 (9)
N3	0.8968 (3)	0.2100 (2)	0.1486 (3)	3.23 (9)
C1	0.7668 (4)	0.1351 (2)	0.1726 (3)	2.9 (1)
C2	0.7362 (4)	0.1491 (3)	0.0718 (3)	3.1 (1)
C3	0.6336 (6)	0.1181 (3)	−0.0115 (4)	4.9 (1)
C4	0.8701 (4)	0.1747 (2)	0.2203 (3)	2.86 (9)
C5	0.9952 (4)	0.2552 (3)	0.1577 (4)	3.8 (1)
C6	1.0908 (5)	0.2640 (4)	0.2462 (4)	4.8 (1)
C7	1.1827 (5)	0.3105 (4)	0.2513 (5)	6.0 (2)
C8	1.1839 (6)	0.3458 (4)	0.1697 (5)	7.0 (2)
C9	1.0900 (6)	0.3349 (4)	0.0829 (5)	8.3 (2)
C10	0.9967 (6)	0.2908 (4)	0.0752 (5)	6.5 (2)
C11	0.8088 (4)	0.0521 (3)	0.4816 (3)	3.3 (1)
C12	0.7001 (5)	0.0170 (3)	0.4645 (3)	3.8 (1)
C13	0.6830 (5)	−0.0263 (3)	0.5348 (4)	4.5 (1)
C14	0.7765 (6)	−0.0363 (3)	0.6243 (4)	5.4 (2)
C15	0.8829 (5)	−0.0015 (3)	0.6437 (4)	4.5 (1)
C16	0.8991 (4)	0.0428 (3)	0.5739 (3)	3.4 (1)
C17	1.0153 (5)	0.0807 (3)	0.5924 (3)	3.6 (1)
C18	0.9466 (6)	0.2068 (3)	0.5697 (4)	5.0 (1)
C19	1.1066 (5)	0.1686 (4)	0.5209 (4)	4.8 (1)
C20	0.5659 (4)	0.1032 (3)	0.2277 (3)	3.3 (1)
C21	0.5446 (5)	0.1545 (3)	0.2884 (4)	4.2 (1)
C22	0.4316 (6)	0.1786 (4)	0.2704 (4)	5.8 (2)
C23	0.3348 (6)	0.1498 (4)	0.1932 (4)	6.0 (2)
C24	0.3554 (6)	0.0993 (4)	0.1344 (5)	5.9 (2)
C25	0.4697 (5)	0.0746 (4)	0.1510 (4)	4.6 (1)
C26	0.7167 (4)	−0.0139 (3)	0.2075 (3)	3.0 (1)
C27	0.6550 (5)	−0.0676 (3)	0.2329 (4)	4.0 (1)
C28	0.6634 (6)	−0.1389 (3)	0.2078 (4)	5.2 (2)
C29	0.7341 (6)	−0.1580 (3)	0.1591 (4)	5.1 (2)
C30	0.7991 (6)	−0.1055 (3)	0.1344 (4)	4.9 (1)
C31	0.7903 (5)	−0.0329 (3)	0.1585 (3)	3.7 (1)
C1S	0.4216 (7)	0.4855 (5)	0.4080 (5)	7.5 (2)
C2S	0.4514 (6)	0.4330 (4)	0.4799 (5)	7.4 (2)
C3S	0.4741 (7)	0.5512 (4)	0.4300 (5)	7.0 (2)

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

Pd—P	2.254 (1)	N1—C17	1.489 (6)
Pd—O	2.140 (3)	N2—N3	1.401 (6)
Pd—N1	2.136 (4)	N2—C2	1.315 (6)
Pd—C11	1.988 (4)	C1—C2	1.419 (6)
P—C1	1.762 (5)	C1—C4	1.388 (6)
P—C20	1.823 (5)	C11—C16	1.400 (7)
P—C26	1.833 (5)	C16—C17	1.502 (7)
O—C4	1.294 (5)		
P—Pd—C11	99.2 (2)	Pd—P—C1	98.5 (2)
O—Pd—N1	91.4 (1)	C26—P—C20	105.6 (2)
C11—Pd—N1	82.6 (2)	P—C1—C4	115.0 (3)
P—Pd—O	86.76 (9)	C1—C4—O	129.6 (4)
Pd—C11—C16	112.6 (4)	C4—O—Pd	110.0 (3)
C11—C16—C17	117.0 (4)	O—C4—N3	123.7 (4)
C16—C17—N1	110.3 (4)	C4—N3—N2	110.5 (4)
C17—N1—Pd	104.2 (3)	C1—C2—C3	127.1 (4)

The title compound was prepared in an atmosphere of dry argon using Schlenk tube techniques. To a THF (tetrahydrofuran) solution of $[Pd(\mu\text{-}Cl)(o\text{-}C_6H_4CH_2NMe_2)]_2$ (Cope & Friedrich, 1968) was added a THF solution of $Na[Ph_2P\{C{=}C(O)N(Ph)N{=}C(Me)\}]$ (1 eq. palladium dimer to 2 eq. *L*Na). After 15 h the mixture was filtered through a glass fritt and concentrated. Pentane was added and a yellow product was precipitated which was recrystallized from a toluene-pentane solution (yield 80%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene-CH_2Cl_2 solution of the complex. IR(KBr): 1596 (*m*), 1585 (*ms*), 1530 (*s*), 1502 (*s*), 1455 (*m*), 1417 (*s*/*br*), 1375 (*s*) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.08-6.72 (19H, aromatic H), 3.96 [*d*, 2H, NCH_2, $^4J(PH)$ = 1.7 Hz], 2.90 [*d*, 6H, NMe_2, $^4J(PH)$ = 2.3 Hz], 1.89 (*s*, 3H, methyl group of pyrazole ring). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 7.0 (*s*). A single air-stable prismatic crystal was used for data collection.

Data collection was carried out using a scan width of $(1 + 0.35\tan\theta)^\circ$ and a variable scan rate with a maximum scan time of 60 s per reflection. After Lorentz and polarization corrections, the crystal structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1983) which revealed some non-H atoms. The remaining non-H atoms of the structure were found after successive scale-factor refinements and difference Fourier syntheses. After isotropic refinement, a benzene molecule appeared, located on a centre of inversion. The whole structure was refined by full-matrix least-squares techniques. H atoms were included in the structure-factor calculations. Their coordinates were chosen to give acceptable stereochemistry (C—H = 0.95 Å) and they were assigned isotropic displacement parameters of B = 5.0 $Å^2$. The *MolEN* (Fair, 1990) package was used for computations.

Lists of structure factors, general and refined displacement parameter expressions for U and B, H-atom coordinates, bond distances and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71443 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1045]

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