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JL313-1

X-ray Structure Determination of {2-[(Methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-8-yl)]-1,10-phenanthroline}[(1,2,3-η)-propenyl]palladium(II) Tetrafluoroborate (31A). MoKα radiation was used on an Enraf-Nonius CAD4 diffractometer operating at 294±1 K. A transparent colorless rod-shaped single crystal of approximate dimensions 0.15 x 0.21 x 0.50 mm and of formula $C_{28}H_{27}PdON_2^+BF_4^-\cdot 0.5H_2O\cdot 0.5CH_2Cl_2$ had triclinic cell parameters *a* = 11.3833 (15), *b* = 11.6038 (19), *c* = 11.6891 (17) Å, α = 71.110 (17)°, β = 66.797 (13)°, γ =79.472 (13)°, and calculated volume V = 1340.0 (3) Å^3. For Z = 2 and formula weight = 652.22 Daltons, the calculated density was 1.62 g/cm^3. The space group was assumed to be *P1* (No. 2), a choice supported by the subsequent successful solution and refinement of the structure. A total of 13,010 reflections were collected, of which 7331 were unique. Lorentz, polarization, and empirical absorption corrections were applied to the data. The structure was solved by direct methods[59] which provided coordinates for all the non-hydrogen atoms of the cation except C-1 and C-25. These two atoms and the atoms of the BF_4^- were located from a difference electron density Fourier map based on the coordinates of the initial 30 atoms. A difference electron density Fourier map calculated after preliminary isotropic refinement revealed a CH_2Cl_2 of solvation disordered across an inversion center as well as positions for several of the hydrogen atoms. After further refinement, a difference electron density Fourier map revealed a second minor position for C-27, the central allyl carbon, and a partially occupied water position. Occupancy refinements on C-27 and C-27' indicated a ratio of 3:1. The occupancy of the water oxygen was set at 0.50. Idealized positions for all hydrogen atoms except the allyl CH2 hydrogens, which were taken from the difference electron density Fourier map, and the water hydrogens, which were not found or included, were calculated (d [C-H] = 0.98 Å; B[H] = 1.1 B[$C_{attached}$]) and the hydrogen atoms were included as fixed contributions. The structure was refined by a full-matrix least-squares process. Scattering factors were taken from Cromer and Waber.[60] Anomalous dispersion effects were included in Fc[3]; the

values for Δf' and Δf" were those of Cromer.[61] Only the 5,991 reflections having intensities greater than 3.0 times their standard deviation (on F_o) were used in the remainder of the refinements. Refinement converged with unweighted and weighted agreement factors of R_1 =0.037 and R_2 = 0.047, and an estimated standard deviation of an observation of unit weight of 1.69. The largest peaks in the final difference electron density Fourier map were near the BF_4^- anion. The highest was 0.74 $e^-/Å^3$ with an estimated error based on ΔF[62] of 0.07. It is probable that there is at least one minor orientation of the anion which was not characterized. This observation is consistent with the finding of a partially occupied water molecule hydrogen bonded to F-4. All calculations were performed using SDP/VAX.[63]

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Table 4. Crystal Data and Intensity Data Collection Parameters for **31A**

Parameter	Value
empirical formula	$C_{28}H_{27}PdON_2^+$ $BF_4^-\cdot 0.5H_2O\cdot 0.5CH_2Cl_2$
formula weight, Daltons	652.22
crystal dimensions, mm	0.15 x 0.21 x 0.50
crystal color/shape	transparent colorless rod
temperature, deg K	294±1
crystal system	triclinic
space group	*P 1* (No. 2)
a, Å	11.3833 (15)
b, Å	11.6038 (19)
c, Å	11.6891 (17)
α,°	71.110(17)
β, °	66.797 (13)
γ, °	79.472 (13)
V, Å^3	1340.0 (3)
lattice parameter refinement	24 reflns; 21.2° < 2Θ < 28.4°
Z	2
calculated density, g/cm^3	1.62
μ (MoKα), cm^{-1}	8.37
diffractometer	Enraf-Nonius CAD4
radiation	graphite crystal, incident beam monochromated MoKα, λ=0.71073 Å
attenuator	Zr foil, factor 19.3
take-off angle, deg	2.8
detector aperture, mm	horizontal 1.8-2.0

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	vertical 4.0
crystal-detector distance, cm	21
omega width at half-height, deg	0.25
scan type	Θ/2Θ
scan rate, deg/min in omega	2.06-5.49
scan width, deg	0.80+0.344tanΘ
2Θ range, deg	3.0 to 58.7
sinΘ/λ maximum	0.689
data total measured	13010
unique measured	7331
unique $F_o > 3\sigma(F_o)$	5991
corrections, on I	Lorentz-polarization
	absorption (transmission: 0.924 to 1.000)
(5552 multiply measured)	R_{merge} (F)= 0.024
refinement	full-matrix least-squares
hydrogen atom	idealized; d[CH]=0.98Å; B [H] =1.1 B [$C_{attached}$]
minimization function	$\Sigma w(\|F_o\|-\|F_c\|)^2$
p, weight= $[\sigma^2(F)^2 + p^2F^2]^{-1/2}$	0.03
anomalous dispersion	all non-hydrogen atoms
data:variable ratio	15.8
discrepancy indices, R_1	0.037
R_2	0.047
goodness of fit	1.69
convergence, largest shift/error	1.22 for β_{11} of Cls1
	0.02 for non CH_2Cl_2 atoms
highest peak in final diff. map	0.74 (7)
computer hardware	VAX station 3200
computer software	SDP/VAX

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Table 5. Selected Interatomic Distances (Å) for **31A**[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Pd	N1	2.101(2)	C15	C16	1.383(4)
Pd	N2	2.141(2)	C16	C17	1.376(3)
Pd	C26	2.136(3)	C17	C18	1.397(3)
Pd	C27	2.115(3)	C17	C22	1.496(3)
Pd	C28	2.114(3)	C18	C19	1.509(3)
Pd	C27'	2.15(1)	C19	C20	1.535(3)
N1	C1	1.332(3)	C19	C24	1.540(3)
N1	C5	1.341(3)	C19	O	1.418(3)
C1	C2	1.381(4)	C20	C21	1.528(4)
C2	C3	1.365(4)	C21	C22	1.537(4)
C3	C4	1.418(4)	C22	C23	1.511(4)
C4	C5	1.413(3)	C23	C24	1.542(4)
C4	C9	1.404(4)	O	C25	1.418(3)
C5	C6	1.438(3)	C26	C27	1.362(5)
C6	N2	1.363(3)	C27	C28	1.337(5)
C6	C7	1.406(3)	C26	C27'	1.24(2)
N2	C12	1.336(3)	C28	C27'	1.36(2)
C7	C8	1.420(3)	B	F1	1.284(4)
C7	C10	1.410(4)	B	F2	1.349(5)
C8	C9	1.338(4)	B	F3	1.304(5)
C10	C11	1.365(3)	B	F4	1.293(5)
C11	C12	1.405(3)	F4	Ow	2.34(1)
C12	C13	1.484(3)	Ow	Ow	2.79(2)
C13	C14	1.409(3)	C29	Cls1	1.84(1)
C13	C18	1.397(3)	C29	Cls2	1.65(1)
C14	C15	1.368(3)			

[a]Estimated standard deviations in the least significant digits are given in parentheses.

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Table 6. Selected Interatomic Angles (in deg)[a] for the Non-Hydrogen Atoms of **31A**

Atom 1	Atom 2	Atom3	Angle	Atom 1	Atom2	Atom 3	Angle
N1	Pd	N2	79.16(7)	C12	C13	C14	118.1(2)
N1	Pd	C26	170.0(1)	C12	C13	C18	123.5(2)
N1	Pd	C27	135.7(1)	C14	C13	C18	118.4(2)
N1	Pd	C28	102.4(1)	C13	C14	C15	121.0(2)
N1	Pd	C27'	136.3(5)	C14	C15	C16	120.1(2)
N2	Pd	C26	109.7(9)	C15	C16	C17	120.2(2)
N2	Pd	C27	142.6(1)	C16	C17	C18	120.4(2)
N2	Pd	C28	176.7(1)	C16	C17	C22	126.0(2)
N2	Pd	C27'	140.1(4)	C18	C17	C22	113.5(2)
Pd	N1	C1	127.7(2)	C13	C18	C17	119.8(2)
Pd	N1	C5	113.6(1)	C13	C18	C19	127.6(2)
C1	N1	C5	118.7(2)	C17	C18	C19	112.6(2)
N1	C1	C2	122.7(3)	C18	C19	C20	108.3(2)
C1	C2	C3	119 6(3)	C18	C19	C24	106.5(2)
C2	C3	C4	119.7(2)	C18	C19	O	107.8(2)
C3	C4	C5	116.3(2)	C20	C19	C24	108.8(2)
C3	C4	C9	123.7(2)	C20	C19	O	111.7(2)
C5	C4	C9	120.1(2)	C24	C19	O	113.5(2)
N1	C5	C4	123.1(2)	C19	C20	C21	110.2(2)
N1	C5	C6	117.9(2)	C20	C21	C22	109.6(2)
C4	C5	C6	119.0(2)	C17	C22	C21	107.7(2)
C5	C6	N2	117 8(2)	C17	C22	C23	108.4(2)
C5	C6	C7	119.0(2)	C21	C22	C23	108.3(2)
N2	C6	C7	123.1(2)	C22	C23	C24	110.4(2)

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Pd	N2	C6	111.5(1)	C19	C24	C23	109.1(2)
Pd	N2	C12	130.4(1)	C19	O	C25	117.5(2)
C6	N2	C12	118.1(2)	C26	C27	C28	124.6(4)
C6	C7	C8	119.3(2)	C26	C27'	C28	133.(1)
C6	C7	C10	117.3(2)	F1	B	F2	109.5(4)
C8	C7	C10	123.4(2)	F1	B	F3	113.3(4)
C7	C8	C9	121.7(2)	F1	B	F4	104.4(4)
C4	C9	C8	120.9(2)	F2	B	F3	107.6(3)
C7	C10	C11	119.2(2)	F2	B	F4	107.8(5)
C10	C11	C12	120.2(2)	F3	B	F4	114.1(4)
N2	C12	C11	121.9(2)	B	F4	Ow	142.3(5)
N2	C12	C13	119.7(2)	F4	Ow	Ow	58.3(3)
C11	C12	C13	118.3(2)	Cls1	C29	Cls2	107.4(6)

[a]Estimated standard deviations in the least significant digits are given in parentheses

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Table 7. Torsional Angles (in deg) for **31A**[a]

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
N2	Pd	N1	C1	175.63(26)	C5	C6	C7	C10	-179 21(26)
N2	Pd	N1	C5	1.01(18)	N2	C6	C7	C8	177.46(27)
C26	Pd	N1	C1	21.71(86)	N2	C6	C7	C10	-1.55(41)
C26	Pd	N1	C5	-154.93(71)	Pd	N2	C12	C11	-177.25(20)
C27	Pd	N1	C1	-20.14(35)	Pd	N2	C12	C13	-0.35(36)
C27	Pd	N1	C5	163.22(24)	C6	N2	C12	C11	4.23(37)
C28	Pd	N1	C1	-1.37(29)	C6	N2	C12	C13	-178.87(22)
C28	Pd	N1	C5	178.00(21)	C6	C7	C8	C9	-1.56(49)
C27'	Pd	N1	C1	17.05(68)	C10	C7	C8	C9	177.40(33)
C27'	Pd	N1	C5	-159.59(63)	C6	C7	C10	C11	2.38(46)
N1	Pd	N2	C6	2.06(16)	C8	C7	C10	C11	-176.60(32)
N1	Pd	N2	C12	-176.54('3)	C7	C8	C9	C4	1.37(53)
C26	Pd	N2	C6	177.42(14)	C7	C10	C11	C12	-0.06(70)
C26	Pd	N2	C12	-1.18(26)	C10	C11	C12	N2	-3.41(45)
C27	Pd	N2	C6	-159.71(26)	C10	C11	C12	C13	179.64(28)
C27	Pd	N2	C12	21.69(36)	N2	C12	C13	C14	-88.89(32)
C28	Pd	N2	C6	120.8(19)	N2	C12	C13	C13	93.38(33)
C28	Pd	N2	C12	-57.7(13)	C11	C12	C13	C14	88.12(34)
C27'	Pd	N2	C6	158.91(67)	C11	C12	C13	C18	-89.61(34)
C27'	Pd	N2	C12	-19.69(71)	C12	C13	C14	C15	-179.14(28)
N1	Pd	C26	C27	-50.17(86)	C18	C13	C14	C15	-1.29(45)
N1	Pd	C26	C27'	-5.8(11)	C12	C13	C18	C17	179.35(26)
N2	Pd	C26	C27	157.13(25)	C12	C13	C18	C19	0.64(44)
N2	Pd	C26	C27'	-158.49(78)	C14	C13	C18	C17	1.62(40)
C27	Pd	C26	C27'	-44.38(80)	C14	C13	C18	C19	-177.09(2)
C28	Pd	C26	C27	-25.87(28)	C13	C14	C15	C16	-0.34(50)
C28	Pd	C26	C27	18.51(79)	C14	C15	C16	C17	1.64(49)
C27'	Pd	C26	C27	44.38 (80)	C15	C16	C17	C18	-1.28(46)
N1	Pd	C27	C26	169.03(20)	C15	C16	C17	C22	177.20(30)
N1	Pd	C27	C28	31.58(39)	C16	C17	C18	C13	-0.37(42)
N1	Pd	C27	C27'	105.0(10)	C16	C17	C18	C9	178.52(26)
N2	Pd	C27	C26	-37.07(40)	C22	C17	C18	C13	-179.03(26)
N2	Pd	C27	C28	-174.52(23)	C22	C17	C18	C19	-0.14(34)
N2	Pd	C27	C27'	-101.1(10)	C16	C17	C22	C21	122.94(33)
C26	Pd	C27	C28	-137.45(44)	C16	C17	C22	C23	-120.15(33)
C26	Pd	C27	C27'	-64.0(10)	C18	C17	C22	C21	-58.49(34)
C28	Pd	C27	C26	137.45(44)	C18	C17	C22	C23	58.42(32)
C28	Pd	C27	C27'	73.4(10)	C13	C18	C19	C20	-123.37(30)
C27'	Pd	C27	C26	64.0(10)	C13	C18	C19	C24	119.81(30)
C27'	Pd	C27	C28	-73.4(10)	C13	C18	C19	O	-2.32(38)
N1	Pd	C28	C27	-158.00(38)	C17	C18	C19	C20	57.84(29)
N1	Pd	C28	C27'	158.91(71)	C17	C18	C19	C24	-58.98(31)
N2	Pd	C28	C27	83.8(19)	C17	C18	C19	O	178.89(23)
N2	Pd	C28	C27'	40.7(21)	C18	C19	C20	C21	-54.89(31)
C26	Pd	C28	C27	26.14(22)	C24	C19	C20	C21	60.43(32)
C26	Pd	C28	C27'	16.91(71)	O	C19	C20	C21	-173.48(25)
C27	Pd	C28	C27'	-43.09(74)	C18	C19	C24	C23	59.20(31)
C27'	Pd	C28	C27	43 09(74)	C20	C19	C24	C23	-57.27(31)
N1	Pd	C27'	C26	178.55(29)	O	C19	C24	C23	177.66(24)

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N1	Pd	C27'	C27	102.22(93)	C18	C19	O	C25	172.54(27)
N1	Pd	C27'	C28	-30.60(99)	C20	C19	O	C25	-68.61(34)
N2	Pd	C27'	C26	32.5(11)	C24	C19	O	C25	54.85(35)
N2	Pd	C27'	C28	176.60(22)	C20	C21	C22	C17	57.59(35)
C26	Pd	C27'	C27	79.2(10))	C20	C21	C22	C23	-59.37(35)
C26	Pd	C27'	C28	150.8(11)	C17	C22	C23	C24	-54.11(33)
C27	Pd	C27'	C26	-79.2(10)	C21	C22	C23	C24	62.42(34)
C27	Pd	C27'	C28	71.62(94)	C22	C23	C24	C19	-3.55(36)
C28	Pd	C27'	C26	-150.8(11)	Pd	C26	C27	C28	51.19(44)
C28	Pd	C27'	C27	-71.62(94)	Pd	C26	C27	C27'	87.2(10)
Pd	N1	C1	C2	-176.25(24)	C27'	C26	C27	Pd	-87.2(10)
C5	N1	C1	C2	0.24(45)	C27'	C26	C27	C28	-36.0(10)
Pd	N1	C5	C4	177.57(20)	Pd	C26	C27'	C27	-78.55(81)
Pd	N1	C5	C6	-0.19(30)	Pd	C26	C27'	C28	-38.4(13)
C1	N1	C5	C4	0.60(39)	C27	C26	C27'	Pd	78.55(81)
C1	N1	C5	C6	-177.16(25)	C27	C26	C27'	C28	40.1(11)
N1	C1	C2	C3	-0.42(50)	Pd	C27	C28	C27'	84.82(97)
C1	C2	C3	C4	-0.23(48)	C26	C27	C28	Pd	-51.45(43)
C2	C3	C4	C5	0.97(42)	C26	C27	C28	C27'	33.3(10)
C2	C3	C4	C9	179.76(30)	C27'	C27	C28	Pd	-84.82(97)
C3	C4	C5	N1	-1.19(39)	Pd	C27	C27'	C26	75.29(50)
C3	C4	C5	C6	176.55(25)	Pd	C27	C27'	C28	-73.93(38)
C9	C4	C5	N1	179.97(46)	C26	C27	C27'	Pd	-75.29(50)
C9	C4	C5	C6	-2.28(40)	C26	C27	C27'	C28	-149.22(81)
C3	C4	C9	C8	-178.15(32)	C28	C27	C27'	Pd	73.93(38)
C5	C4	C9	C8	0.59(48)	C28	C27	C27'	C26	149.22(81)
N1	C5	C6	N2	2.13(35)	Pd	C28	C27'	C26	39.1(14)
N1	C5	C6	C7	179.91(23)	Pd	C28	C27'	C27	81.45(77)
C4	C5	C6	N2	-175.72(23)	C27	C28	C27'	Pd	-81.45(77)
C4	C5	C6	C7	2.06(37)	C27	C28	C27'	C26	-42.3(12)
C5	C6	N2	Pd	-2.84(27)	F2	B	F1	F4	115.20(65)
C5	C6	N2	C12	175.95(22)	F3	B	F1	F4	-124.68(72)
C7	C6	N2	Pd	179.47(21)	F2	B	F4	F1	-116.38(57)
C7	C6	N2	C12	-1.73(37)	F3	B	F4	F1	124.18(67)
C5	C6	C7	C8	-0.19.(41)					

[a]Estimated standard deviations in the least significant digits are given in parentheses.

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Table 8. Fractional Triclinic Cooordinates and Isotropic Displacement Parameters (Å^2)[a] for the Non-hydrogen Atoms of **31A**

Atom	*x*	*y*	*z*	B_{iso}
Pd	0.79588(2)	0.29647(2)	0.10644(2)	3.457(4)
N1	0.9351(2)	0.3898(2)	-0.0649(2)	3.75(5)
C1	0.9199(3)	0.4558(3)	-0.1755(3)	4.71(8)
C2	1.0203(3)	0.5078(3)	-0.2849(3)	5.15(9)
C3	1.1407(4)	0.4926(3)	-0.2813(3)	5.31(9)
C4	1.1613(3)	0.4240(2)	-0.1653(3)	4.23(7)
C5	1.0526(3)	0.3735(2)	-0.0594(2)	3.52(6)
C6	1.0684(2)	0.2973(2)	0.0588(2)	3.36(5)
N2	0.9636(2)	0.2431(2)	0.1565(2)	3.14(4)
C7	1.1908(3)	0.2786(3)	0.0669(3)	4.12(7)
C8	1.2957(3)	0.3349(3)	-0.0416(3)	5.19(8)
C9	1.2817(3)	0.4033(3)	-0.1527(3)	5.08(8)
C10	1.2025(3)	0.2021(3)	0.1838(3)	4.78(8)
C11	1 0975(3)	0.1468(3)	0.2805(3)	4.40(7)
C12	0.9793(2)	0.1663(2)	0.2634(2)	3.37(5)
C13	0.8680(2)	0.1037(2)	0.3709(2)	3.29(5)
C14	0.7927(3)	0.1626(2)	0.4668(3)	4.15(7)
C15	0.6898(3)	0.1092(3)	0.5694(3)	4.46(7)
C16	0.6577(3)	-0.0041(3)	0.5800(3)	4.18(7)
C17	0.7309(2)	-0.0650(2)	0.4892(3)	3.62(6)
C18	0.8367(2)	-0.0121(2)	0.3842(2)	3.23(5)
C19	0.9067(2)	-0.0940(2)	0.2974(2)	3.59(6)
C20	0.8118(3)	-0.1243(3)	0.2493(3)	4.70(7)
C21	0.6944(3)	-0.1790(3)	0.3641(3)	5.41(8)
C22	0.7111(3)	-0.1898(3)	0.4914(3)	4.47(7)
C23	0.8305(3)	-0.2706(3)	0.4954(3)	5.11(9)
C24	0.9495(3)	-0.2124(3)	0.3828(3)	4.63(7)
0	1.0100(2)	-0.0307(2)	0.1935(2)	4.55(5)
C25	1.0986(4)	-0.0962(4)	0.1080(4)	6.6(1)
C26	0.6371(3)	0.2026(4)	0.2592(4)	5.85(9)
C27	0.5935(4)	0.3064(4)	0.1877(5)	5.4(1)
C28	0.6293(3)	0.3383(4)	0.0586(4)	6.3(1)
C27'	0.609(1)	0.235(1)	0.160(2)	6.1(4)
B	0.3285(4)	0.5888(5)	0.3129(4)	6.1(1)
F1	0.2106(3)	0.5927(3)	0.3882(4)	11.7(1)
F2	0.3490(3)	0.5026(3)	0.2515(3)	11.6(1)
F3	0.3628(5)	0.6918(4)	0.2245(4)	17.7(2)
F4	0.3916(4)	0.5531(7)	0.3905(4)	23.1(2)
Ow	0.4671(9)	0.6038(9)	-0.4556(9)	12.8(3)
C29	0.4440(9)	0.9466(9)	0.0663(8)	8.5(3)
Cls1	0.4297(2)	1.0434(2)	-0.0875(2)	7.89(7)
Cls2	0.5497(2)	1.0054(3)	0.0921(2)	11.08(8)

[a]Estimated standard deviations in the least significant digits are given in parentheses. Thermal parameters for the anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) $[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$