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Registry No. *mer*-W(CO)$_3$(P(OMe)$_3$)(η^4-1,5-cyclooctadiene), 128190-45-4; *fac*-W(CO)$_3$(P(OMe)$_3$)(η^4-1,5-cyclooctadiene), 128298-34-0; W(CO)$_5$(P(OMe)$_3$), 23306-42-5.

Supplementary Material Available: Tables of the hydrogen atom positional and thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, complete bond distances and angles, and torsional angles (5 pages); a listing of observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of a Biphenanthrol–Palladium Complex Displaying an Unusual Bonding Mode

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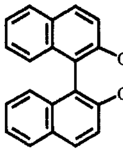
Summary: The dipotassium salt of 10,10′-dihydroxy-9,9′-biphenanthryl reacts with [Pd(CH$_3$CN)$_4$]$^{2+}$ to give a complex in which the ligand is bound to palladium by an oxygen atom and the 9′-position carbon atom. The properties and X-ray structure of this unusual compound are described. Crystal data for C$_{32}$H$_{22}$N$_2$O$_2$Pd; monoclinic, $P2_1/c$, a = 9.022 (1) Å, b = 18.054 (3) Å, c = 15.778 (2) Å, β = 104.25 (1)°, V = 2490.9 (9) Å^8, Z = 4, $R(F)$ = 4.77%. Reasons are suggested for this binding, which may be general for these types of ligands bound to group 8 metals.

The chiral molecule 2,2′-dihydroxy-1,1′-binaphthyl (1) and its derivatives have been used extensively in asymmetric synthesis and in the study of chiral recognition. As examples of asymmetric synthesis we note the highly enantioselective reduction of ketones,[1] the highly stereoselective thiirane polymerization,[2] and the enantioselective cyclization of unsaturated aldehydes.[3] Complexes of 1 incorporating the Lewis acid metals boron,[4] titanium,[5] and aluminum[6] have promoted or catalyzed the Diels–Alder reaction with high enantioselectivity. Alkyltitanium complexes of ligand 1 are effective enantioselective alkyl-transfer reagents to ketones.[7] In all of these examples the metal complexes were generated in situ and the identity of the species in solution was left undetermined. It was assumed, however, that 1 binds to the metal via the two (deprotonated) oxygen atoms to form a seven-membered chelate ring. Similar, though less extensive, studies[8,9] have been carried out with the analogous ligand 10,10′-dihydroxy-9,9′-biphenanthryl (2, biph(H)$_2$). We considered using 2 coordinated to palladium(II) for asymmetric catalytic Claisen rearrangements.[10] The complex formed by the reaction of 2 with palladium is unusual and unexpected.



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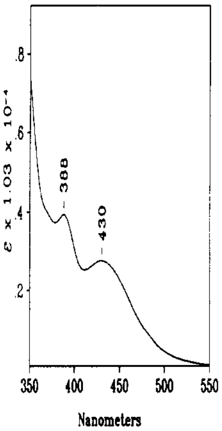
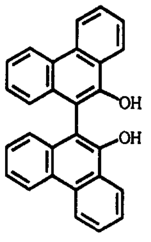


Figure 1. Electronic absorption spectrum of [Pd(biph)(CH$_3$CN)$_2$] in acetonitrile solution.



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1. Synthesis and Properties of [Pd(biph)(CH$_3$CN)$_2$]

When 1 equiv of the dipotassium salt of 2 is allowed to react with [Pd(CH$_3$CN)$_4$](NO$_3$)$_2$ in acetonitrile solution, dark brown-red crystals of a compound analyzed as [Pd(biph)(CH$_3$CN)$_2$] can be isolated. The compound is

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Table I. Crystallographic Data for $C_{32}H_{22}N_2O_2Pd$

(a) Crystal Parameters

formula	$C_{32}H_{22}N_2O_2Pd$	V, Å^3	2490.9 (9)
space	$P2_1/c$	Z	4
group	monoclinic	cryst dimens, mm	0.10 × 0.08 × 0.09
cryst syst	9.022 (1)	cryst color	red
a, Å	18.054 (3)	D(calc), g cm^{-3}	1.528
b, Å	15.778 (2)	μ(Mo Kα), cm^{-1}	7.56
c, Å	104.25 (1)	temp, °C	23
β, deg			

(b) Data Collection

diffractometer	Nicolet R3m
monochromator	graphite
scan technique	Wyckoff
radiation	Mo Kα (λ = 0.71073 Å)
2θ scan range, deg	4–46
scan speed, deg min^{-1}	5–20 (variable)
no. of rflns collected	3623
no. of indep rflns.	3359
R(merg), %	2.37
no. of obsd rflns $F_o > 5\sigma(F_o)$	1994
std rflns	3 std/197 rflns
var in stds, %	<1

(c) Refinement

$R(F)$, %	4.77	Δ/ρ, e Å^{-3}	0.399
$R(wF)$, %	4.86	GOF	1.097
Δ/σ(max)	0.011	N_o/N_v	5.97

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U[a]
Pd	6292.8 (8)	904.3 (4)	8628.3 (5)	45.1 (2)
O(1)	6940 (6)	307 (3)	7744 (4)	56 (2)
O(2)	7039 (7)	2424 (3)	7502 (4)	59 (2)
N(1)	4548 (8)	121 (4)	8586 (5)	62 (3)
N(2)	5520 (8)	1482 (4)	9528 (5)	54 (3)
C(1)	3568 (10)	−281 (5)	8515 (6)	59 (4)
C(2)	2302 (10)	−782 (6)	8432 (7)	84 (5)
C(3)	4972 (10)	1793 (5)	9979 (6)	56 (4)
C(4)	4285 (12)	2209 (7)	10579 (7)	98 (6)
C(5)	7455 (8)	2289 (4)	8279 (5)	39 (3)
C(6)	7197 (9)	2814 (4)	8944 (6)	50 (3)
C(7)	6210 (11)	3408 (5)	8683 (7)	70 (4)
C(8)	5943 (11)	3929 (5)	9272 (7)	81 (5)
C(9)	6608 (11)	3840 (6)	10130 (8)	90 (5)
C(10)	7593 (11)	3265 (6)	10429 (7)	73 (5)
C(11)	7933 (10)	2738 (4)	9843 (5)	47 (3)
C(12)	9013 (10)	2133 (5)	10122 (5)	48 (3)
C(13)	9949 (10)	2085 (5)	10980 (5)	56 (4)
C(14)	10944 (10)	1521 (5)	11236 (6)	64 (4)
C(15)	11052 (10)	956 (5)	10664 (5)	59 (4)
C(16)	10146 (9)	983 (5)	9811 (5)	49 (3)
C(17)	9124 (9)	1560 (4)	9526 (5)	42 (3)
C(18)	8182 (8)	1559 (4)	8606 (5)	42 (3)
C(19)	8226 (10)	552 (5)	7572 (5)	49 (3)
C(20)	8859 (10)	137 (5)	6971 (5)	50 (3)
C(21)	8117 (12)	−509 (5)	6591 (6)	69 (4)
C(22)	8744 (12)	−911 (6)	6012 (7)	82 (5)
C(23)	10057 (15)	−678 (6)	5820 (7)	95 (6)
C(24)	10776 (13)	−56 (6)	6176 (7)	79 (5)
C(25)	10244 (11)	377 (5)	6779 (5)	56 (4)
C(26)	10981 (9)	1031 (5)	7185 (5)	49 (3)
C(27)	12383 (10)	1290 (6)	7053 (6)	73 (4)
C(28)	13105 (10)	1919 (6)	7470 (7)	73 (5)
C(29)	12423 (11)	2301 (6)	8028 (6)	64 (4)
C(30)	11086 (10)	2073 (5)	8186 (5)	51 (3)
C(31)	10334 (9)	1435 (5)	7790 (5)	45 (3)
C(32)	8916 (9)	1181 (4)	7956 (5)	45 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

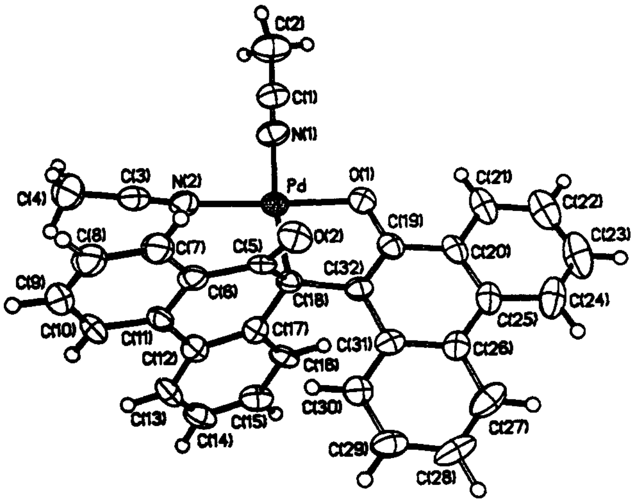

Figure 2. Molecular structure and labeling scheme for $C_{32}H_{22}N_2O_2Pd$. Ellipsoids are drawn to 35% probability (bond radius 0.040 Å).

Table III. Bond Distances and Angles for $C_{32}H_{22}N_2O_2Pd$

(a) Bond Distances (Å)

Pd–O(1)	1.962 (6)	O(1)–C(19)	1.330 (11)
Pd–N(1)	2.104 (7)	O(2)–C(5)	1.215 (9)
Pd–N(2)	2.018 (8)	C(19)–C(32)	1.363 (11)
Pd–C(18)	2.082 (8)	C(18)–C(32)	1.513 (12)
N(1)–C(1)	1.128 (12)	C(5)–C(18)	1.506 (11)
N(2)–C(3)	1.114 (13)		

(b) Bond Angles (deg)

O(1)–Pd–N(1)	87.7 (3)	O(1)–Pd–N(2)	176.7 (3)
N(1)–Pd–N(2)	89.1 (3)	O(1)–Pd–C(18)	84.9 (3)
N(1)–Pd–C(18)	171.9 (3)	N(2)–Pd–C(18)	98.3 (3)
Pd–O(1)–C(19)	112.9 (5)	Pd–N(1)–C(11)	175.8 (7)
Pd–N(2)–C(3)	174.0 (7)	N(1)–C(1)–C(2)	178.9 (11)
N(2)–C(3)–C(4)	178.7 (10)	O(2)–C(5)–C(18)	121.4 (7)
Pd–C(18)–C(5)	102.3 (5)	Pd–C(18)–C(17)	104.9 (5)
Pd–C(18)–C(32)	104.6 (5)	O(1)–C(19)–C(32)	120.8 (8)
C(18)–C(32)–C(19)	116.7 (8)		

sparingly soluble in most common solvents; in DMF solution ^{1}H NMR spectroscopy indicates that the coordinated acetonitrile ligands are replaced by DMF. Acetonitrile solutions are stable indefinitely but in CH_2Cl_2 or $CHCl_3$ solutions the brown-red compound is converted to an as yet unidentified violet species.

The visible absorption spectrum of [Pd(biph)$(CH_3CN)_2$] in acetonitrile solution is shown in Figure 1; absorption bands at 430 and 388 nm are probably d–d transitions. The ^{1}H NMR spectrum was unexpected and indicated that the ligand is devoid of a 2-fold rotation axis; all aromatic protons are inequivalent (see Experimental Section).

2. Crystal Structure

Crystals of racemic [Pd(biph)$(CH_3CN)_2$] were obtained from acetonitrile solution by vapor diffusion with ether.[11] Experimental details are given in Table I and positional and thermal parameters in Table II. The structure is shown in Figure 2, where the unusual coordination of the ligand is clearly evident. Table III lists some of the relevant bond distances and bond angles. These appear unexceptional, except we note that the Pd–N(1) bond length is longer than Pd–N(2), presumably due to the

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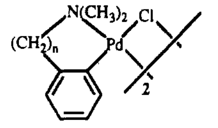
(11) Crystal data for $C_{32}H_{22}N_2O_2Pd$: monoclinic, $P2_1/c$, a = 9.022 (1) Å, b = 18.054 (3) Å, c = 15.778 (2) Å, β = 104.25 (1)°, V = 2490.9 (9) Å^3, Z = 4, μ(Mo Kα) = 7.65 cm^{-1}, D(calcd) = 1.528 g cm^{-3}, 23 °C, Nicolet R3m diffractometer, graphite monochromator. The crystal (0.10 × 0.08 × 0.09 mm) was mounted on a glass fiber. A total of 3623 reflections were collected ($4° \le 2\theta \le 46°$); 3359 were independent (R_{merg} = 2.37%), and 1994 were observed with $F_o > 5\sigma(F_o)$. No absorption correction was applied (small crystal, low μ). The structure was solved by direct methods, which located the Pd atom. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms are isotropic, fixed, and idealized. $R(F)$ = 4.77%, $R(wF)$ = 4.86%, GOF = 1.097, $\Delta\rho$ = 0.399 e Å^{-3}, Δ/σ(max) = 0.011, and N_o/N_v = 5.97. SHELXTL (5.1) software was used for all computations (G. Sheldrick, Nicolet XRD, Madison, WI).

greater trans effect of the Pd–C(18) bond.

3. Discussion

The origins of the unusual coordination of the biph ligand to palladium(II) probably reside in a number of concerted factors. Were the ligand to bind by the two anionic oxygen atoms, an O–Pd–O angle of ≤90° would engender strain in the ligand system. Assuming a Pd–O bond length of ~2.0 Å, molecular models suggest that a bite angle of >90° is required to strainlessly accommodate ligand coordination. Consistently, the O–Ti–O angle of (ethylenebis(4,5,6,7-tetrahydro-(*S*)-indenyl))titanium (*S*)-1,1'-bi-2-naphtholate (an analogue of [Cp_2TiX_2]) is 94.4°.[12] The inherently larger bite angle of this class of complex and the oxophilic character of titanium(IV) probably both contribute to formation of the seven-membered chelate ring. Palladium(II), however, is neither oxophilic nor is a bite angle of >90° normally observed for first-row donor atoms. In general, palladium(II) prefers bite angles of <90°, which are formed by five-membered chelate rings. The classical ortho-metalation product **3**, which bears some analogy to the present compound, was found to occur only when $n = 1$; no ortho metalation was observed when $n = 0$, 2, or 3.[13]



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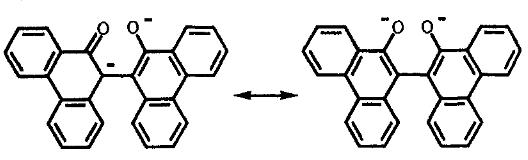
In addition to these steric and electronic factors there is an electronic property associated with polyaromatic systems that also contributes to the stability of the metal–carbon bond in the present system. This is related to the relative stabilities of the keto–enolate forms of the biph ligand, **4** and **5**. That the dianionic keto form **4** is an energetically accessible structure is supported by the chemistry of the analogous dianion of **1**.[14] Thus, the major product of the reaction of ethylene glycol ditosylate with the dianion, 1,1'-binaphthyl 2,2'-dioxide is **7**, presumably via the intermediacy of the keto anion **6**. Similarly, 1-substituted 2-naphthol anions alkylate at the C-1 position under anhydrous conditions.[15] The keto form **4** of the biph ligand is expected to be even more stable than that of the naphtholate anions because the loss of aromaticity is expected to be less.



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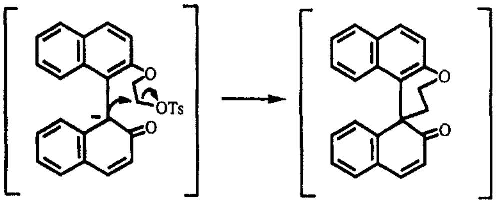

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Thus, in our judgment, the unusual structure of [Pd(biph)(CH_3CN)$_2$] arises principally from the steric constraints of the ligand, the stability of the keto form, and the fact that palladium(II) is not an oxophilic metal. We suspect that the present structure may be representative of a class of structures which will form with group 8 metals incorporating bis(polyaromatic biphenols), of which biph is one member and the dianion of the binaphthol **1** is another.

4. Experimental Section

The racemic ligand, 10,10'-dihydroxy-9,9'-biphenanthryl[8] and [Pd(CH_3CN)$_2$$Cl_2$][16] were prepared by reported methods. ^1H NMR spectra were obtained on a 500-MHz spectrometer, and the UV spectra were recorded on a Varian (Cary) 2400 spectrophotometer. Elemental analyses were performed by Huffman Laboratories, Golden, CO.

[Pd(biph)(CH_3CN)$_2$]. The initial part of this reaction was carried out under argon. To a solution of [Pd(CH_3CN)$_2$$Cl_2$] (0.3 g, 1.16 mmol) in acetonitrile (50 mL) was added dropwise a solution of $AgNO_3$ (0.396 g, 2.32 mmol) in acetonitrile (15 mL). After it was stirred for 1 h at 25 °C, the mixture was filtered through a Celite plug with use of a cannula. The dipotassium salt of 10,10'-dihydroxy-9,9'-biphenanthryl **2** (0.535 g, 1.16 mmol), prepared by adding solid **2** (0.446 g, 1.16 mmol) to a solution of KO-*t*-Bu (0.259 g, 2.32 mmol) in dry THF (30 mL), was added to the yellow filtrate over 5 min. A dark brown-red solution and precipitate formed immediately. After the mixture was stirred for 20 min, the solvent was removed and the resulting brown residue was extracted with CH_2Cl_2 (200 mL) and quickly filtered through Celite. The filtrate was evaporated to dryness. The residue was dissolved in hot acetonitrile (50 mL). Soon after dissolution of the residue, brown-red crystals of the product began to form. The mixture was allowed to stand and cool to 25 °C for 1 h. The air-stable brown-red crystals of [Pd(biph)(CH_3CN)$_2$] were collected, washed with ether, and dried in a desiccator; yield 0.40 g, 60%. Anal. Calcd for $C_{32}H_{22}N_2O_2Pd$: C, 67.1; H, 3.9; N, 4.9. Found: C, 65.9; H, 3.9; N, 5.4. ^1H NMR (CD_3CN, TMS (external)): δ 8.60 (d, $J = 8.8$ Hz, 1 H), 8.48 (d, $J = 8.8$ Hz, 1 H), 8.34 (d, $J = 7.9$ Hz, 1 H), 8.32 (d, $J = 9.4$ Hz, 1 H), 8.23 (d, $J = 6.9$ Hz, 1 H), 8.18 (d, $J = 9.1$ Hz, 1 H), 7.73 (t, $J = 6.6$ Hz, 1 H), 7.68 (m, 3 H), 7.38 (d, $J = 7.2$ Hz, 1 H), 7.33 (t, $J = 7.6$ Hz, 1 H), 7.07 (m, 2 H), 6.90 (t, $J = 6.0$ Hz, 1 H), 6.18 (d, $J = 7.3$ Hz, 1 H). The CH_3CN ligand resonances were obscured by the solvent peak. UV (CH_3CN solution): 388 nm ($\epsilon = 3807$), 430 nm ($\epsilon = 2673$).

Acknowledgment. This work was supported by grants from the National Institutes of Health.

Supplementary Material Available: Listings of bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates (4 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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