Photochemical synthesis and thermal interconversion of mer- and fac-W(CO)3(P(OMe)3(.eta.4-1,5-cyclooctadiene)

Donald J. Wink, and Chang Kyeong Oh

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Reactions of Complexes. A Schlenk tube containing 70 mg (0.17 mmol) of 7 was immersed in an oil bath. After the sample was heated at 210 °C for 3 h, the thermolysis product was analyzed by GLC, which showed formation of 64 mol % of 3-butenamide and 6 mol % of 2-butenamide based on 7. Other reactions listed in Table III were carried out under conditions shown in the table.

Supplementary Material Available: Figure S1, showing the molecular structure of 2, and Tables S1–S3, giving atomic coordinates and equivalent isotropic temperature factors, anisotropic thermal factors, and bond distances and angles (10 pages); Table S4, giving observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Notes

Photochemical Synthesis and Thermal Interconversion of *mer*- and *fac*-$W(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-cyclooctadiene})$

Donald J. Wink* and Chang Kyeong Oh

Department of Chemistry, New York University, New York, New York 10003

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Summary: Both *fac* and *mer* isomers of $W(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-cyclooctadiene})$ are formed in a photolysis reaction. They readily interconvert thermally, with the *fac* isomer favored by a ca. 2:1 ratio.

Group 6 pseudooctahedral olefin complexes are an important source of novel coordination stoichiometries and geometries.[1] Several early studies showed a general preference for $M(CO)_4$ derivatives to bind nonconjugated dienes,[2] but we have recently shown that this preference is *inverted* in the case of the $Cr(CO)_3(P(OMe)_3)$ fragment.[3] Our initial speculation was that the inversion was caused by electronic factors; that is, the phosphite adds enough additional electron density to the metal to make the fragment prefer a conjugated diene, which is a superior π-acceptor, instead of a nonconjugated diene, which is a superior σ-donor.[4] However, a single metal ligand environment is insufficient to test this, and we have therefore moved down the triad to tungsten, where steric effects should be minimized and back-bonding emphasized. This paper reports our results, including the photochemical synthesis of both the *mer* and the *fac* isomers of the parent $W(CO)_3(P(OMe)_3)(\eta^4\text{-1,5-cyclooctadiene})$ and the determination that the inversion observed with chromium is, in fact, due to *electronic* factors.

Results and Discussion

Irradiation of a pentane solution of $W(CO)_5(P(OMe)_3)$ and 1,5-cyclooctadiene (COD) with the apparatus externally cooled by dry ice produces a mixture of the meridional and facial isomers of tricarbonyl(cyclooctadiene)(trimethyl phosphite)tungsten(0) (eq 1).

$$\begin{aligned}&W(CO)_5(P(OMe)_3) + 1,5\text{-}C_8H_{12} \xrightarrow{h\nu}\\ &\qquad mer\text{-}W(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) +\\ &\qquad\qquad fac\text{-}W(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) \quad (1)\end{aligned}$$

The components of the reaction mixture are separated by column chromatography on silica with use of a column cooled by a water jacket. Elution with 10:1 pentane–ether is sufficient to separate the two isomers, and a single crystallization renders them spectroscopically pure of minor side products. Final purification of analytically pure materials is accomplished by crystallization of yellow needles from pentane.

The identity of the two isomers is determined by NMR and IR spectroscopy. The *mer* isomer exhibits an NMR spectrum quite similar to that observed for the chromium congener (the sole exception being among the aliphatic hydrogens of cyclooctadiene, where there is greater resolution with Cr, presumably due to the proximity of certain hydrogens to the metal). However, the spectrum of the *fac* isomer contains resonances for the olefinic protons that are much closer together and, more importantly, that show a strong cross peak in a COSY spectrum. This indicates that the protons are in similar, spin-coupled environments and is consistent with the *fac* isomer with the COD ligand asymmetric with respect to a mirror plane *through the C–C double bonds*. In addition, the ^{13}C spectrum of the *mer* complex contains two well-separated resonances, at δ 89.2 and 75.2, assigned to the C=C bonds trans to CO and phosphorus, respectively. For the *fac* complex the olefin resonances are much closer together, at δ 86.3 and 82.4. The infrared spectra of the two complexes are also consistent with the assigned geometry.[5] The *fac* isomer exhibits three strong bands at 1980, 1915, and 1870 cm^{-1}, while localized C_{2v} symmetry in the *mer* isomer yields three bands at 2000 (w), 1920 (s), and 1880 (m) cm^{-1}.

The *fac* geometry was confirmed by a solid-state structural study. Experimental details are provided in Table I, positional and isotropic thermal parameters for

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Table I. Experimental Details for Crystallographic Study

A. Crystal Data	
empirical formula	$C_{14}H_{21}O_6PW$
fw	500.14
habit	yellow block
size, mm	0.30 × 0.30 × 0.40
cryst syst	monoclinic
lattice params	a = 10.070 (6) Å b = 14.835 (6) Å c = 11.797 (6) Å β = 105.35 (4)°
V, Å^3	1699 (2)
space group	$P2_1/n$ (No. 14)
Z	4
systematic absences	$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$
B. Intensity Measurements	
diffractometer	Rigaku AFC6S
radiation (λ, Å)	Mo Kα (0.71069)
temp, °C	−80
scan type	ω–2θ
scan rate, deg min^{-1}	4.0
F_{000}	968
μ(Mo Kα), cm^{-1}	70.82
$2\theta_{max}$, deg	60.1
data collected	$+h,+k,\pm l$
no. of rflns measd	5082
no. of unique rflns (R_{int})	4856 (0.046)
transmissn factors for abs cor	0.88–1.10
C. Structure Solution and Refinement	
no. of observns ($I > 3.00\sigma(I)$)	3733
no. of variables	200
no. of rflns/variable	18.7
residuals, %	R = 3.1, R_w = 4.3
goodness of fit	1.25
max peak in final diff map, e Å^{-3}	2.0
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, $w = 4F_o^2/\sigma^2(F_o)$

Table II. Positional and Isotropic Thermal Parameters for $W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene)

atom	x	y	z	B(eq), Å^2
W	0.45154 (2)	0.19362 (1)	0.17106 (2)	1.524 (9)
P	0.3408 (1)	0.3406 (1)	0.1731 (1)	1.81 (4)
O1	0.4358 (4)	0.4236 (3)	0.2307 (4)	2.9 (2)
O2	0.2577 (4)	0.3750 (3)	0.0451 (3)	2.4 (1)
O3	0.2294 (4)	0.3479 (3)	0.2468 (4)	2.2 (1)
O4	0.1642 (5)	0.1293 (4)	0.0206 (4)	3.6 (2)
O5	0.3880 (5)	0.1722 (3)	0.4155 (4)	3.3 (2)
O6	0.5217 (6)	−0.0113 (3)	0.2063 (5)	4.2 (2)
C1	0.4045 (8)	0.4907 (5)	0.3078 (7)	3.7 (3)
C2	0.1846 (8)	0.4595 (4)	0.0309 (6)	3.3 (3)
C3	0.1070 (7)	0.2927 (4)	0.2189 (6)	2.7 (2)
C4	0.2674 (6)	0.1545 (4)	0.0768 (5)	2.3 (2)
C5	0.4115 (5)	0.1819 (4)	0.3246 (5)	1.9 (2)
C6	0.5012 (7)	0.0629 (4)	0.1916 (5)	2.4 (2)
C11	0.5003 (6)	0.2537 (4)	−0.0020 (5)	2.2 (2)
C12	0.5553 (7)	0.1680 (4)	0.0104 (5)	2.6 (2)
C13	0.7094 (7)	0.1506 (5)	0.0493 (6)	3.4 (3)
C14	0.7725 (6)	0.1412 (5)	0.1816 (6)	3.2 (3)
C15	0.6981 (6)	0.1937 (4)	0.2558 (5)	2.4 (2)
C16	0.6587 (6)	0.2826 (4)	0.2373 (5)	2.4 (2)
C17	0.6923 (6)	0.3407 (5)	0.1426 (6)	2.9 (2)
C18	0.5855 (6)	0.3389 (4)	0.0231 (5)	2.6 (2)

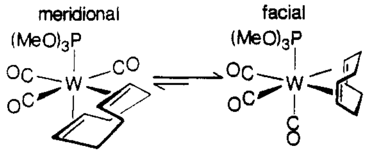
the non-hydrogen atoms are in Table II, and important bond lengths and angles are in Table III. An ORTEP drawing of the molecule, which corresponds to the asymmetric unit, is given in Figure 1. The tungsten to olefinic carbon bonds are essentially equal, in contrast to the shorter metal–olefin bond to the diene segment trans to ethylene in *mer*-$W(CO)_3(\eta^2-C_2H_4)(\eta^4$-norbornadiene)[1b] and trans to the phosphorus in *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-COD)[3] and *mer*-$Cr(CO)_3(PPh_3)(\eta^4$-norbornadiene).[6]

Table III. Selected Intramolecular Distances (Å) and Angles (deg) for $W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene)

W–P	2.452 (2)	O3–C3	1.443 (7)
W–C4	1.980 (6)	O4–C4	1.139 (7)
W–C5	1.965 (5)	O5–C5	1.167 (7)
W–C6	2.001 (6)	O6–C6	1.125 (7)
W–C11	2.395 (5)	C11–C12	1.379 (9)
W–C12	2.424 (6)	C15–C16	1.378 (9)
W–C15	2.419 (6)	W–C16	2.417 (6)
W–CentA[a]	2.31	W–CentB[a]	2.32
P–W–C4	84.6 (2)	P–W–C5	82.2 (2)
P–W–C6	163.8 (2)	C4–W–C5	95.9 (2)
C4–W–C6	87.2 (3)	C5–W–C6	84.7 (2)
W–C4–O4	177.1 (6)	W–C5–O5	178.0 (5)
W–C6–O6	175.3 (6)	CentA–W–CentB	77.3
CentA–W–P	99.5	CentB–W–P	98.5
CentA–W–C4	91.5	CentB–W–C4	168.7
CentA–W–C5	172.6	CentB–W–C5	95.3
CentA–W–C6	94.7	CentB–W–C6	92.3

[a] CentA refers to the center of the C11–C12 bond. CentB refers to the center of the C15–C16 bond.

Thermal equilibration of the isomers takes place in C_6D_6 by heating either isomer in the presence of additional COD above 60 °C.[7] The equilibrium [*fac*]:[*mer*] ratio at 85 °C is 2.4 (2), corresponding to a free energy for the *mer* to *fac* isomerization (eq 2) of −0.6 (1) kcal mol^{-1}. The equilibrium constant is almost unaffected by temperature, suggesting that there is a negligible entropy change for the reaction (ΔS° = +3 (3) eu and, therefore, ΔH° = −0.6 (1) kcal mol^{-1}). The rate of isomerization is independent of the actual concentration of added diene. This is similar to the results obtained by Rousche and Dobson for the effect of added triisopropyl phosphite on the *fac* to *mer* isomerization of $Mo(CO)_3(dppe)(P(OPr^i)_3)$,[8] although in that case there is no mention of the rate in the absence of added ligand.



(2)

Both *mer* and *fac* isomers of $W(CO)_3(P(OMe)_3)(\eta^4$-1,5-COD) react with isoprene in C_6D_6 to form *fac*-$W(CO)_3(P(OMe)_3)(\eta^4$-isoprene), previously reported by Kreiter.[9] The *fac* isomer reacts considerably faster than the *mer* species, and the *fac* isomer can be selectively substituted in a mixture of the two isomers if the temperature is kept below 60 °C. The corresponding chromium complex also undergoes rapid stereospecific substitution by trimethyl phosphite at room temperature in C_6D_6.[3] Neither of the tungsten isomers undergoes such a reaction *at room temperature*. However, both react with $P(OMe)_3$ at elevated (70 °C) temperatures. The *fac* complex reacts much faster than the *mer*, and the evidence suggests, qualitatively, that *mer* to *fac* isomerization occurs prior to or in competition with substitution.

Except where steric crowding is important, octahedral zerovalent group 6 tricarbonyl complexes of π-acids exhibit a strong thermodynamic preference for the *fac* isomer,[10]

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(6) Declercq, J. P.; Germain, G.; van Meersche, M.; Chawdury, S. A. *Acta Crystallogr.* **1975**, *B31*, 2896.

(7) The isomerization reaction takes much longer in the absence of added COD, and decomposition occurs. Similarly, photolysis of a C_6D_{12} solution of the complexes results in immediate decomposition to unidentified materials (the corresponding *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^6$-1,5-cyclooctadiene) complex can be converted photochemically to the agostic complex $Cr(CO)_2(P(OMe)_3)(\eta^1(CH)-\eta^4$-1,3-cyclooctadiene): Wink, D. J. Unpublished results.

(8) Rousche, J.-C.; Dobson, G. R. *Inorg. Chim. Acta* **1978**, *28*, L139.

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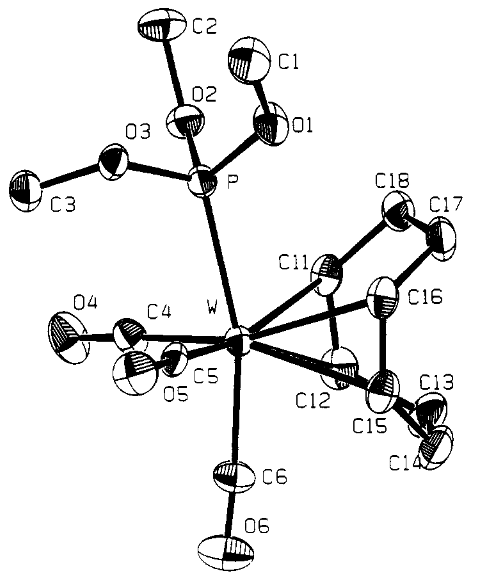

Figure 1. ORTEP drawing of the solid-state structure of the *fac* isomer, with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

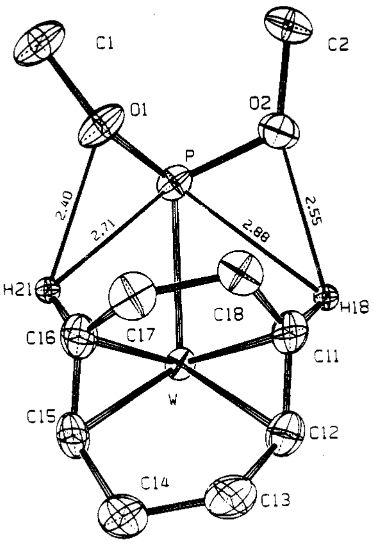

Figure 2. Drawing illustrating the contact between the hydrogens on the olefin groups and the phosphite ligand.

though the *mer* isomer can often be prepared kinetically. It is rare to find both *fac* and *mer* complexes in equilibrium with one another. Here, we believe the *fac* complex is observed because there is just barely enough room for the COD ligand in that orientation. There are two very close intramolecular contacts between olefin hydrogens and the phosphite oxygens (Figure 2). With the chromium congener the metal to ligand bonds would be about 0.15 Å shorter and, we suggest, the olefin–phosphite crowding would prevent the formation of *fac*-$Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene).

Experimental Section

General Considerations. Pentane for photolysis reactions was treated with H_2SO_4, dried over K_2CO_3, and distilled from CaH_2. Solvents for chromotography were anhydrous grade, used as supplied. Pentacarbonyl(trimethyl phosphite)tungsten(0) was made by photolysis of $W(CO)_6$ (Pressure) in THF followed by addition of $P(OMe)_3$ and crystallization. Cyclooctadiene (Aldrich, redistilled grade) was used as supplied. All NMR data were obtained in C_6D_6 (Aldrich) on General Electric QE-300 or GN-300 instruments operating at 300.1 MHz (^1H), 75.4 MHz (^{13}C), and 121.5 MHz (^{31}P). Infrared data were obtained on a Mattson Polaris FTIR instrument.

Synthesis of *mer*- and *fac*-Tricarbonyl(η^4-cyclooctadiene)(trimethyl phosphite)tungsten(0). A solution of 4 g of pentacarbonyl(trimethyl phosphite)tungsten (8.9 mmol) in 500 mL of pentane was photolyzed for 2 h in the presence of 1.0 g of 1,5-cyclooctadiene (10 mmol). The reaction mixture was cooled by cooling water through the immersion well and by *solid* dry ice packing on the outside of the reactor. A 450-W Hg lamp (Ace) was used.

The crude reaction mixture was separated into its components by column chromatography on silica gel (230–400 mesh). Elution with 10:1 pentane–ether gives a wide yellow band. The first third of the band was collected and reduced in volume by approximately 50% to give a first crop of 0.786 g (18%) of yellow microcrystalline *mer*-$W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene). The supernatant was then chilled to give yellow microcrystalline solids identified as a mixture of *mer* complex and $W(CO)_4(\eta^4$-1,5-COD). The second third of the band on the column was collected to give a small amount of a mixture of *fac* and *mer* isomers. The last part of the band gave a crude product upon concentration to 50% of its volume; recrystallization from pentane yields 0.20 g (5%) of *fac*-$W(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene). The supernatant contains a small amount of what is tentatively identified as $W(CO)_2(P(OMe)_3)_2(\eta^4$-1,5-COD).

Spectroscopic and analytical data for the *mer* isomer: ^1H NMR δ 4.2–4.0 m (4 H, $=CH$), 3.4 (9 H, d, $P(OCH_3)_3$), 2.5–2.2, 2.2–2.0 (8 H, m, CH_2); ^{13}C NMR δ 217.4 (d, $J_{PC} = 5$ Hz, CO trans to olefin), 214.8 (d, $J_{PC} = 14$ Hz, CO trans to CO), 89.2 (s, C=C trans to CO), 75.2 (d, C=C trans to phosphite, $J_{PC} = 6$ Hz), 52.0 (d, $P(OCH_3)_3$, $J_{PC} = 5$ Hz), 31.7 and 30.3 (s, CH_2); ^{31}P NMR (relative to external H_3PO_4) δ 154.1. Anal. Calcd for $C_{14}H_{21}O_6W$: C, 33.42; H, 4.20. Found: C, 33.76; H, 4.78.

Spectroscopic and analytical data for the *fac* isomer: ^1H NMR δ 4.4–4.3 (2 H, m, $=CH$), 4.0–3.8 (2 H, m, $=CH$), 3.4 (9 H, d, $P(OCH_3)_3$), 2.4–2.15, 2.15–2.0, 1.9–1.7 (8 H, m, CH_2); ^{13}C NMR δ 217.3 (d, $J_{PC} = 28$ Hz, CO trans to phosphite), 212.7 (d, $J_{PC} = 15$ Hz, CO trans to olefin), 86.3 (s, C=C), 82.4 (s, C=C), 52.3 (d, $P(OCH_3)_3$, $J_{PC} = 6$ Hz), 31.5 (s, CH_2); ^{31}P NMR (relative to external H_3PO_4) δ 145.8. Anal. Calcd for $C_{14}H_{21}O_6W$: C, 33.42; H, 4.20. Found: C, 33.46; H, 4.46.

X-ray Crystallography. A tabulation of most of the experimental details is provided in Table I. The crystals were mounted on a glass fiber under a flow of cold nitrogen gas and then transferred to the goniostat, which was equipped with a flow of nitrogen regulated at −80 °C. Cell constants and an orientation matrix for data collection were obtained from the setting angles of 25 reflections in the range $30.0 < 2\theta < 35.0°$. The Laue group was confirmed by a check of equivalent reflections. The space group was determined by an examination of systematic absences[11] and confirmed by successful solution and refinement of the structure. There was no significant decay in three check reflections, and the data were used directly. Structure solution was by Patterson methods,[12] to locate the tungsten, followed by a series of least-squares refinements and difference Fourier map analysis to find the remaining non-hydrogen atoms. After isotropic refinement of the structure, an empirical absorption correction was applied.[13]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the

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(10) Leading references include: (a) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727. (b) Bond, A. M.; Colton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 2378. (c) Bond, A. M.; Colton, R.; Kevekordes, J. E. *Inorg. Chem.* **1986**, *25*, 749. (d) Vila, J. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1778.

(11) TEXSAN-TEXRAY Structure Analysis Package; Molecular Structure Corp.: College Station, TX, 1985.

(12) PHASE, Patterson heavy atom solution extractor: Calabrese, J. C. Ph.D. Thesis, University of Wisconsin—Madison, 1972.

(13) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

National Science Foundation for funds to purchase X-ray diffraction equipment (Grant No. CHE87-11307).

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

Steven H. Bergens, Pak-hing Leung, and B. Bosnich*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

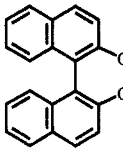
Arnold L. Rheingold

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received February 22, 1990

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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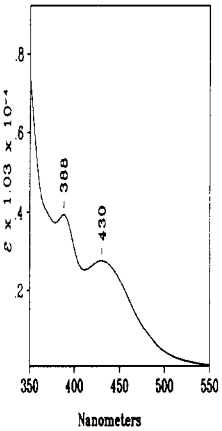
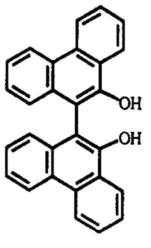


Figure 1. Electronic absorption spectrum of [Pd(biph)(CH$_3$CN)$_2$] in acetonitrile solution.



2

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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