Contribution from the Department of Natural Sciences,
University of Michigan—Dearborn, Dearborn, Michigan 48128

Preparation, Separation, and Characterization of Geometrical Isomers of an Eight-Coordinate Bis(quadridentate Schiff base)tungsten(IV) Complex

CRAIG J. DONAHUE,* DIANE CLARK-MOTIA, and MATTHEW E. HARVEY

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The reaction of a 1 to 2.5 mole ratio of $W(CO)_6$ and *N,N'*-bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (H_2-*t*-Bu_2Me_2dsp) in dry mesitylene at 170 °C under anaerobic conditions produces a complex mixture of more than 15 species. Of the species isolated from the product mixture by preparative TLC, four have been characterized as neutral eight-coordinate bis(quadridentate Schiff base)tungsten(IV) complexes. On the basis of various spectroscopic studies these four complexes are classified as stereoisomers of one another. Labeled α-, β-, γ-, and δ-W(*t*-$Bu_2Me_2dsp)_2$, on the basis of descending order of their R_f values, these complexes have nearly identical visible and infrared spectra. The visible spectrum of each complex in $CHCl_3$ has a band centered around 21 500 cm^{-1} ($\epsilon > 10^4$) and a shoulder at lower energy, 15 700 cm^{-1} ($\epsilon > 10^3$). The former band is assigned as a metal-to-ligand charge-transfer transition and the shoulder as a d–d transition. Four *tert*-butyl signals are observed in the 360-MHz ^1H NMR spectrum of each complex in $CDCl_3$. However, the chemical shift values of these signals are different for each complex. The splitting patterns in the remainder of the ^1H NMR spectra and in the corresponding 90-MHz ^{13}C NMR spectra point to a set of complexes with no inherent symmetry. The possible stereochemistry of the W(*t*-$Bu_2Me_2dsp)_2$ complexes is discussed in terms of Orgel's rule and structures of previously characterized eight-coordinate Zr(IV) and W(IV) complexes.

Introduction

The isolation of eight-coordinate stereoisomers has long been thought to be an unlikely accomplishment.[1] This prediction is based on both theoretical studies and experimental results. Theoretical studies reveal that the two idealized geometries, the D_{4d} square antiprism and the D_{2d} dodecahedron, stabilize eight-donor atoms around a metal center to nearly the same extent.[2] The C_{2v} bicapped trigonal prism is the third structure, along with the dodecahedron and the square antiprism, that has been grouped into a low-energy set of idealized eight-coordinate geometries.[3] It lies on a reaction pathway between the square antiprism and the dodecahedron. Of the early transition-metal eight-coordinate complexes that have been structurally characterized, the vast majority possess either dodecahedral or square antiprismatic geometry. Some complexes that possess bicapped trigonal prismatic geometry are also known.[4] The particular isomeric form that is actually observed in an eight-coordinate complex is determined by a host of factors including electronic, steric, and crystal-packing effects. For chelating ligands the size of the chelate ring and a variable number of bonding modes also become factors. Recent calculations show that for nonchelating ligands polytopal rearrangements are barrierless for at least one pathway between the dodecahedron and the square antiprism.[5] Other calculations by Kepert reveal that even with chelating ligands this energy barrier can be relatively small.[6]

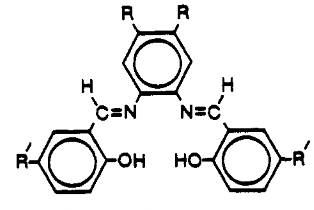
That eight-coordinate isomers are difficult to isolate and sometimes even to detect has been experimentally substantiated. The results of numerous variable-temperature NMR studies[7] reveal that isomeric forms of eight-coordinate complexes can normally be detected only at temperatures substantially below room temperature on the NMR time frame. See Table I.

Only a couple of reports have appeared that describe the actual occurrence of eight-coordinate stereoisomers. In one instance, two isomeric forms of the eight-coordinate complex, $V(S_2CCH_3)_4$, were found to coexist in a single crystal—the expected dodecahedral *mmmm* stereoisomer and the unexpected dodecahedral *mmgg* stereoisomer.[8] However, no details were provided as to the existence or stability of these two stereoisomers in solution.

In another instance, eight-coordinate isomers were isolated from solution. In this study[9] a pair of isomers (designated α and β) were isolated from solution by liquid chromatography for the mixed-ligand eight-coordinate complex, bis(5-methylpicolinato)bis(5,7-dichloro-8-quinolinolato)tungsten(IV), W(mpic)$_2$(dcq)$_2$. Although these isomers were isolatable, they nonetheless would equilibrate back to a mixture of the α and β forms in 24 h at 25 °C when either form was placed back into solution.

In order to further delineate the factors that are necessary for stabilization of eight-coordinate stereoisomers we have initiated a series of studies designed to explore how the nature of the ligand affects the nonrigid/rigid behavior of eight-coordinate tungsten(IV) complexes. Our preliminary assumption was that those ligands that could most effectively enhance the rigid character of this class of eight-coordinate complexes would be flexible, multidentate ligands containing two or more different donor atoms.

One quadridentate ligand that fits the above requirements and has also been demonstrated to stabilize an eight-coordinate complex is *N,N'*-disalicylidene-1,2-phenylenediamine (**1a**). The eight-coordinate complex bis(*N,N'*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(dsp)$_2$, has recently been prepared and fully characterized.[10] For our preliminary study we selected an analogue of **1a**, *N,N'*-bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (**1b**), for use as a ligand.



H_2dsp (1a): R = R' = H
H_2-*t*-Bu_2Me_2dsp (1b): R = Me, R' = *t*-Bu

Here, we report the results of this study, which have led to the separation and characterization of a new set of eight-coordinate stereoisomers obtained from the reaction of tungsten hexacarbonyl and the quadridentate Schiff-base ligand **1b**. Thin-layer chromatographic studies and nuclear magnetic resonance studies indicate these complexes are the most stereochemically rigid

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Table I. Summary of Important Eight-Coordination Nonrigidity Studies

complex	d confign	$\Delta G^{\ddagger}$, kcal/mol	coalesc temp, °C	comments	ref
$Zr(acac)_4$	d^0	7.18	−145	equiv donor atoms	7a
$Zr(Sacac)_4$	d^0		poss coalesc in −141 to −163 °C region	nonequiv donor atoms	7b
$Zr(O_2CNMe_2)_4$	d^0			single methyl ^1H reson down to −120 °C	7c
$Ti(S_2CNMe_2)_4{}^+$	d^0			single methyl ^1H reson down to −90 °C	7d
$Ta(S_2CNMe_2)_4{}^+$	d^0	11.50	−62	equiv donor atoms, pos charge	7e
$Ti(SOCNMe_2)_4$	d^0	9.88	−84	nonequiv donor atoms	7f
$Zr(SOCNMe_2)_4$	d^0	11.25	−54		
$W(CN)_8{}^{4-}$	d^2			single ^{13}C reson to −150 °C; two lines expected for "rigid" dodecahedral struct	7g
$(CH_3NC)_4Mo(CN)_4$	d^2			only two ^{13}C cyanide lines observed down to −47 °C	7h
$H_4Mo[PPh_2Me]_4$	d^2	12.5	−15	molybdenum monodentate complex to tungsten monodentate to tungsten bidentate complex	7i
$H_4W[PPh_2Me]_4$	d^2	14.5	28		
$H_4W[diphos]_2$	d^2	16.5	60		

eight-coordinate isomers yet to be synthesized.

Experimental Section

Solvents and Reagents. Chloroform (Fisher, spectrograde), mesitylene (Eastman), hexamethylenetetramine (Eastman), 4-*tert*-butylphenol (Aldrich), 4,5-dimethyl-*o*-phenylenediamine (Aldrich), tungsten hexacarbonyl (Pressure Chemical), and trimethylamine–borane (Aldrich) were used without further purification.

5-*tert*-Butyl-2-hydroxybenzaldehyde was prepared by the method of Duff.[11] A mixture of glycerol (150.0 g, 1.63 mol) and boric acid (35.0 g, 0.57 mol) contained in a long-neck 500-mL round-bottom flask was heated to 170 °C for several hours to expel the water. The mixture was cooled to 150 °C, and hexamethylenetetramine (25.0 g, 0.18 mol) and 4-*tert*-butylphenol (25.0 g, 0.17 mol) were added in rapid succession. Failure to add the phenol immediately after the addition of the amine resulted in recovery of the reactant only. After a short induction period (5–10 min), the temperature rose abruptly and the flask was intermittently removed from the heat in order to maintain the reaction temperature between 150 and 160 °C. Failure to monitor the reaction, stir the solution, and maintain the desired temperature resulted in the mixture erupting out of the top of the flask. After 30 min of reaction time, the viscous brown mixture was cooled to 110 °C and 125 mL of 6 M H_2SO_4 added. The product was recovered by steam distillation. The product, a pale yellow-green oil, was extracted with ether (3 × 50 mL), the ether dried with anhydrous $MgSO_4$, and the product recovered by flash evaporation. The product was purified by vacuum distillation: bp 124 °C (13 torr); yield 7.0 g (13.5%). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.01; H, 7.75.

***N*,*N*′-Bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene** was prepared by refluxing a mixture of 4,5-dimethyl-*o*-phenylenediamine (1.39 g, 0.01 mol) and 5-*tert*-butyl-2-hydroxybenzaldehyde (3.65 g, 0.02 mol) in 50 mL of absolute ethanol for 1 h. The orange product was recovered by filtration and recrystallized from a 1:1 v/v $CHCl_3$/ethanol mixture: yield 3.6 g (77%); mp 184–186 °C. Anal. Calcd for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95; N, 6.13. Found C, 78.81; H, 7.92; N, 6.09.

W(*t*-Bu$_2$Me$_2$dsp)$_2$ Complexes. Tungsten hexacarbonyl (0.93 g, 2.64 mmol) and *N*,*N*′-bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (3.00 g, 6.57 mmol) were placed in a 200-mL Schlenk flask along with a stirring bar and 70 mL of mesitylene. A Freidrich condenser fitted with an adapter was attached to the flask. The entire system was degassed several times and back-filled with nitrogen. The mixture was heated to 170 °C for 5 h under a nitrogen atmosphere. Upon cooling, the mesitylene and unreacted tungsten hexacarbonyl were removed by vacuum pump assisted rotary evaporation. A dark brown powder was recovered.

Isolation of the W(*t*-Bu$_2$Me$_2$dsp)$_2$ Complexes. Thin-layer chromatography was used to isolate the individual W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes from the product mixture. A total of 16 species were identified in the product mixture. One edge of a precoated silica gel plate (20 × 20 cm, thickness 2.0 mm or 0.25 mm, E. Merck Anal.) was streaked with a concentrated chloroform solution of the product mixture and developed with chloroform as the eluent. The thicker plates were used first to effect a crude separation. The final separation was accomplished with the thinner plates and the following solvents as eluents: α-W(*t*-Bu$_2$Me$_2$dsp)$_2$, 3:1 v/v chloroform/hexanes; β- and γ-W(*t*-Bu$_2$Me$_2$dsp)$_2$, chloroform; δ-W(*t*-Bu$_2$Me$_2$dsp)$_2$, methylene chloride. Typically, four to eight cycles (separation and recovery) were needed to obtain pure material. See Table II for the analyses of the W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes.

Table II. R_f Values, Percent Abundances, and Analyses for the W(*t*-Bu$_2$Me$_2$dsp)$_2$ Complexes

complex	R_f[a]	abund, %	anal.[b] found
α	0.92	~5	C, 65.98; H, 6.33; N, 5.09
β	0.68	~50	C, 65.82; H, 6.26; N, 5.09
γ	0.57	~30	C, 65.44; H, 6.15; N, 5.28
δ	0.29	~15	C, 66.52; H, 6.33; N, 4.36

[a] E. Merck Silica Gel 60 TLC plates, 0.25-mm thickness, were used; eluent was 2:1 v/v chloroform/hexanes. The chloroform was stabilized by 0.75% ethanol. [b] Anal. Calcd for $W(C_{30}H_{34}N_2O_2)_2$: C, 65.93; H, 6.27; N, 5.13.

Reduction of *N*,*N*′-Bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene with Trimethylamine–Borane. Following the procedure of Billman and McDowell,[12] *N*,*N*′-bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (0.45 g, 0.1 mmol) was suspended in 30 mL of glacial acetic acid contained in a 100-mL round-bottom flask. Trimethylamine–borane (0.1 g, 1.4 mmol) dissolved in 30 mL of glacial acetic acid was added dropwise to the stirred Schiff-base solution. The solution was refluxed for 15 min, cooled, and neutralized with 6 M NaOH and the product mixture recovered by filtration. The individual products were isolated by thin-layer chromatography using silica gel plates and chloroform as the eluent. See Table VII and the Results for further details.

Physical Studies. The infrared spectra were recorded on a Perkin-Elmer 283 instrument as KBr disks. The electronic spectra were recorded on a Cary 118 spectrophotometer using a pair of matched 1.000-cm quartz cells. The 60-MHz ^1H NMR spectra were measured on a Varian T-60A spectrometer, and the 360-MHz ^1H NMR and 90-MHz ^{13}C NMR spectra were recorded on a Brucker FT spectrometer. All spectra are referenced to Me_4Si. Mass spectra were recorded on a Finnegan mass spectrometer. Analyses were performed by Spang Microanalytical Laboratory.

Results

Synthesis and Separation of the W(*t*-Bu$_2$Me$_2$dsp)$_2$ Complexes. Oxidative decarbonylation of tungsten hexacarbonyl by the quadridentate Schiff-base ligand **1b** affords a complex mixture of more than 15 products, some of which have been isolated by thin-layer chromatography. Of the species isolated, four analyze as eight-coordinate bis(quadridentate Schiff base)tungsten(IV) complexes, W(*t*-Bu$_2$Me$_2$dsp)$_2$. These complexes have been labeled α-, β-, γ-, and δ-W(*t*-Bu$_2$Me$_2$dsp)$_2$ on the basis of the descending order of their R_f values. See Table II. Thus far we have only been able to isolate the α, β, and γ complexes in an analytically pure state. All of these complexes are brown in color. They are air stable and can be chromatographed repeatedly without decomposition or interconversion. On the basis of examination of

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Table III. Electronic Spectra of the $W(t\text{-}Bu_2Me_2dsp)_2$ Complexes in Chloroform[a]

ligand	complex α	β	γ	δ
36 900 (24 800)	35 000 (34 800)	35 700 (sh, 27 700)	35 300 (sh, 39 700)	36 000 (sh, 25 700)
29 200 (21 000)	28 100 (20 700)	28 300 (22 800)	28 300 (24 200)	28 300 (20 000)
	21 700 (24 000)	21 400 (22 800)	21 500 (26 200)	21 100 (17 000)
	15 300 (sh, 2000)	15 900 (sh, 2300)	16 100 (sh, 3200)	15 400 (sh, 2000)

[a] The values given are in cm^{-1}; the numbers in parentheses are ε values; sh = shoulder. The ε values for $\delta\text{-}W(t\text{-}Bu_2Me_2dsp)_2$ are approximate.

Table IV. Infrared Spectra of the $W(t\text{-}Bu_2Me_2dsp)_2$ Complexes[a]

$H_2\text{-}t\text{-}Bu_2Me_2dsp$	complex α	β	γ	δ	assgnt
2955 s	2958 vs	2948 vs	2953 vs	2962 vs	
2860 m	2865 m	2860 m	2862 m	2864 w	
1617 s	1618 s	1615 s	1617 s	1619 s	ν(C=N)
1582 s					
	1546 m	1543 m	1543 m	1548 w	
1487 s	1488 vs	1488 vs	1486 vs	1492 vs	
1462 w	1465 sh	1465 sh	1465 sh	1462 m	
1391 m					
1363 m	1362 m	1360 m	1360 m	1361 m	
1351 m					
1287 s	1314 m	1310 m	1313 m	1309 m	ν(C—O)
1263 s	1260 vs	1262 vs	1262 vs	1266 vs	
1240 m					
1176 s	1180 m	1180 m	1180 m	1179 w	
1133 m	1125 m	1125 m	1124 w	1127 w	
1080 m					
	1008 m	1010 sh	1008 w	1003 w	
880 m					
870 m					
		834 vs		841 m	
822 s	820 vs	825 vs	828 vs	820 s	
795 w	794 w	794 m	794 w	795 w	
	546 s	544 s	544 m	553 m	
	523 m	520 m	522 w	520 w	

[a] Key: vs = very strong; s = strong; m = medium; w = weak; sh = shoulder. Bands considered weak for all the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are not listed.

the product mixture by TLC, the β and γ complexes are the predominant forms of $W(t\text{-}Bu_2Me_2dsp)_2$. See Table II for relative percentages.

Electronic Absorption Spectra. The electronic absorption spectra of the α-, β-, γ-, and $\delta\text{-}W(t\text{-}Bu_2Me_2dsp)_2$ complexes in chloroform are nearly superimposable upon one another. See Figure 1. Table III summarizes the maxima observed for the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes along with those observed for the parent ligand, **1b**. The electronic spectra of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are characterized by an intense band at approximately 21 500 cm^{-1} and a much weaker band at approximately 15 800 cm^{-1}. The electronic spectrum of these complexes also contains two intense bands present in the UV region. These later two bands are also present in the spectrum of the Schiff-base ligand **1b**. The maxima of these bands are shifted between 1000 and 2000 cm^{-1} to lower energy on complexation.

Infrared Spectra. As is the case with the electronic spectra, the infrared spectra of the four $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are nearly superimposable upon one another. Nearly all the major peaks found in the infrared spectrum of one complex are present within ±5 cm^{-1} in the spectrum of the other three complexes. Table IV summarizes the important infrared bands of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes, as well as those found for **1b**. Absent from the IR spectrum of all of the complexes are bands in the CO metal carbonyl stretching region. While the C=N stretch of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes relative to that of the parent ligand, **1b**, is unchanged, the phenolic, C—O stretch is shifted approximately 25 cm^{-1} from 1287 to near 1312 cm^{-1} upon chelation.

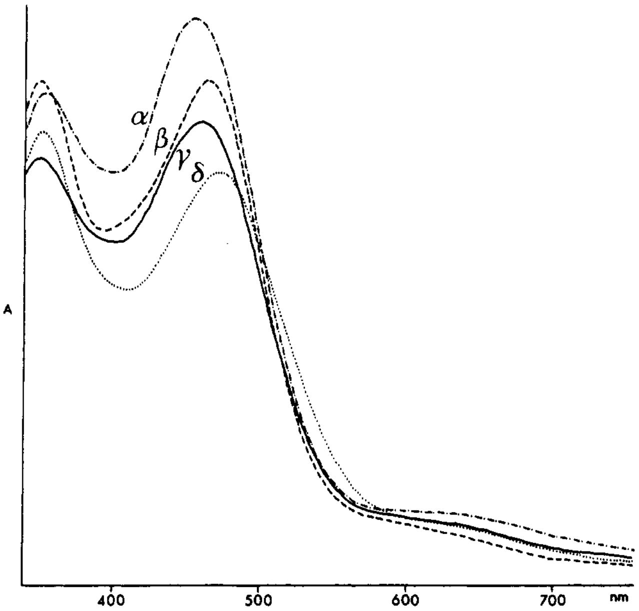

Figure 1. Visible spectrum of the α-, β-, γ-, and $\delta\text{-}W(t\text{-}Bu_2Me_2dsp)_2$ complexes in $CHCl_3$.

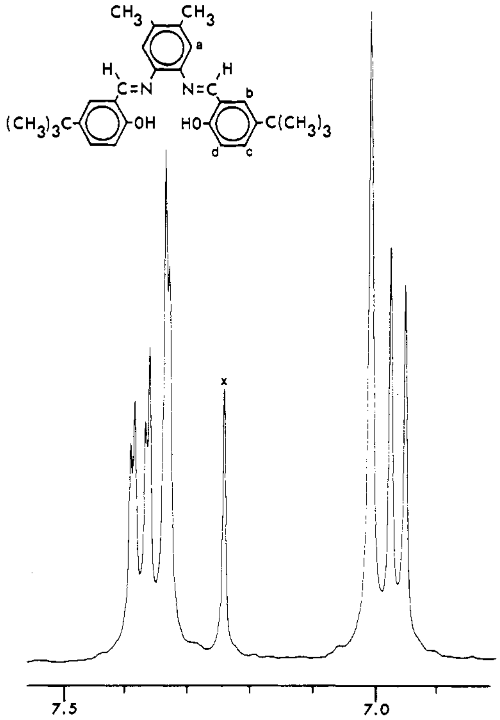

Figure 2. 360-MHz ^1H NMR spectrum, 7.0–7.5 ppm, of *N,N′*-bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (**1b**) in $CDCl_3$ (x = $CHCl_3$).

^1H NMR Spectra. The 360-MHz ^1H NMR spectrum of **1b** in $CDCl_3$ consists of singlets at 1.30, 2.32, 8.62, and 12.95 ppm with relative intensities of 9, 3, 1, and 1. These peaks are assigned to the hydrogens of the *tert*-butyl, methyl, aldimine, and phenol groups, respectively. At high resolution the aromatic hydrogens are readily distinguishable, giving rise to a simple first-order spectrum. See Figure 2. The pair of hydrogens on the phenylenediamine ring, H_a, give rise to a singlet. The aromatic

Table V. 360-MHz ^{1}H NMR Spectrum of the Free Ligand and the α-, β-, γ- and δ-W(t-Bu$_2$Me$_2$dsp)$_2$ Complexes in CDCl$_3$[a] at 35 °C

compd	t-Bu	Me	H$_a$	H$_b$[b]	H$_c$[c]	H$_d$[d]	aldimine[e]	phenolic
1b	1.30 s (9)	2.32 s (3)	7.01 s (1)	7.33 d (1)	7.38 dd (1)	6.96 d (1)	8.62 s (1)	12.95 s (1)
α complex[f]	0.92 s (9)	1.75 s (3)	6.46 s (1)	6.31 d (1)	6.42 dd (1)	5.99 d (1)	5.40 s (1)	
	1.19 s (9)	2.14 s (3)		7.06 d (1)	6.96 dd (1)	6.18 d (1)	6.14 s (1)	
	1.25 s (9)	2.53 s (6)		7.22 d (1)	7.38 dd (1)	6.27 d (1)	6.22 s (1)	
	1.28 s (9)					6.49 d (1)	8.29 s (1)	
β complex[g]	0.28 s (9)	1.91 s (3)	6.90 s (1)	7.19 d (1)	6.78 dd (1)	6.44 d (1)	5.69 s (1)	
	1.29 s (9)	2.27 s (3)	6.93 s (1)	7.33 d (1)	6.98 dd (1)	6.51 d (1)	5.95 s (1)	
	1.30 s (9)	2.30 s (3)		7.41 d (1)	7.05 dd (1)	6.54 d (1)	6.22 s (1)	
	1.31 s (9)	2.49 s (3)			7.37 dd (1)		8.14 s (1)	
γ complex[h]	0.72 s (9)	1.74 s (3)	6.85 s (1)	6.35 d (1)	6.93 dd (1)	6.06 d (1)	5.20 s (1)	
	0.94 s (9)	2.18 s (3)	6.98 s (1)	7.26 d (1)	7.21 dd (1)	6.21 d (1)	6.24 s (1)	
	1.24 s (9)	2.55 s (3)		7.29 d (1)	7.36 dd (1)		8.31 s (1)	
	1.31 s (9)	2.58 s (3)			7.40 dd (1)			
δ complex[i]	1.23 s (9)	1.90 s (3)	6.64 s (1)	7.19 d (1)	6.79 dd (1)	6.31 d (1)	5.66 s (1)	
	1.27 s (9)	2.25 s (3)	6.72 s (1)	7.33 d (1)	6.99 dd (1)	6.34 d (1)	6.04 s (1)	
	1.31 s (9)	2.29 s (3)	6.74 s (1)	7.42 d (1)	7.29 dd (1)	6.45 d (1)	6.48 s (1)	
	1.34 s (9)	2.31 s (3)	6.96 s (1)			6.55 d (1)	8.08 s (1)	

[a] Resonance signals reported in ppm downfield from tetramethylsilane. Key: s, singlet; d, doublet; dd, a doublet of doublets. Relative integrated intensities in parentheses. [b] J_{bc} is consistently 2.2 ± 0.3 Hz for both ligand and complexes. [c] J_{cb} and J_{cd} are consistently 2.3 ± 0.2 and 8.4 ± 0.3 Hz, respectively, for both ligand and complexes. [d] J_{dc} is consistently 8.5 ± 0.2 Hz for both ligand and complexes. [e] Those singlets in the W(t-Bu$_2$Me$_2$dsp)$_2$ complex spectra that fall closest to the free-ligand value of 7.01 ppm are assigned as H$_a$ hydrogens; the remainder are assigned as aldimine hydrogens. [f] Unresolved multiplets are also present at 6.72 and 6.62 ppm. [g] Unresolved multiplets are also present at 6.30 and 6.62 ppm. [h] Unresolved multiplets are also present at 6.54 and 6.78 ppm. [i] An unresolved multiplet is also present at 7.06 ppm.

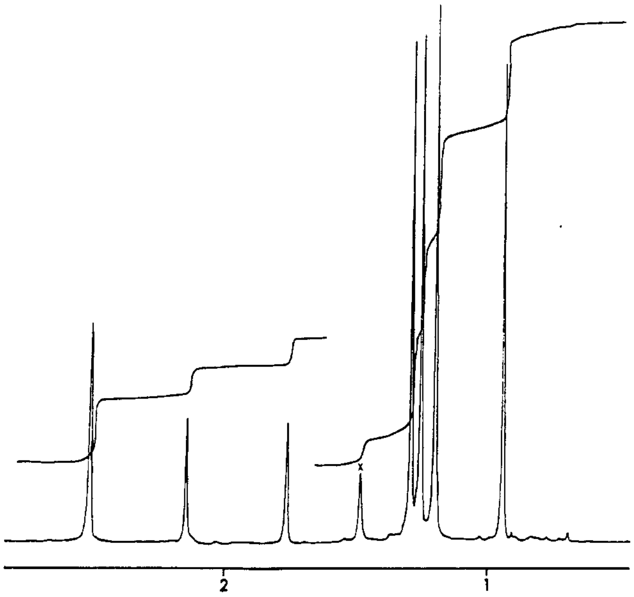

Figure 3. 360-MHz ^{1}H NMR spectrum, 0–3 ppm, of α-W(t-Bu$_2$Me$_2$dsp)$_2$ in CDCl$_3$ at 35 °C (X = impurity).

hydrogens ortho to the aldimine group, H$_b$, appear as a doublet; the aromatic hydrogens ortho to the *tert*-butyl group and meta to the hydroxy group, H$_c$, appear as a doublet of doublets; and the aromatic hydrogens ortho to the hydroxy group, H$_d$, also appear as a doublet. The H$_b$ and H$_c$ signals appear together near 7.35 ppm while the H$_a$ and H$_d$ signals appear together near 7.00 ppm. See Table V for chemical shift values and coupling constants.

The 360-MHz ^{1}H NMR spectrum of each W(t-Bu$_2$Me$_2$dsp)$_2$ complex contains four unique *tert*-butyl signals. See Table V and Figures 3–5. In no instance, however, are the four chemical shift values associated with the four *tert*-butyl peaks for one complex the same as the set of values obtained for the other complexes. Several of the *tert*-butyl signals associated with the W(t-Bu$_2$Me$_2$dsp)$_2$ complexes are shifted upfield from the typical range for a *tert*-butyl signal. This occurrence is most striking in the β-W(t-Bu$_2$Me$_2$dsp)$_2$ complex, which has three t-butyl signals at 1.30 ± 0.01 ppm while the fourth *tert*-butyl signal occurs as a broad singlet at 0.28 ppm. The ^{1}H NMR spectrum of each W(t-Bu$_2$Me$_2$dsp)$_2$ complex also reveals a unique pattern for the methyl groups. For the β, γ, and δ complexes all four methyl groups give rise to a unique peak. For the α-W(t-Bu$_2$Me$_2$dsp)$_2$ complex a pair of methyl groups are equivalent or accidentally equivalent.

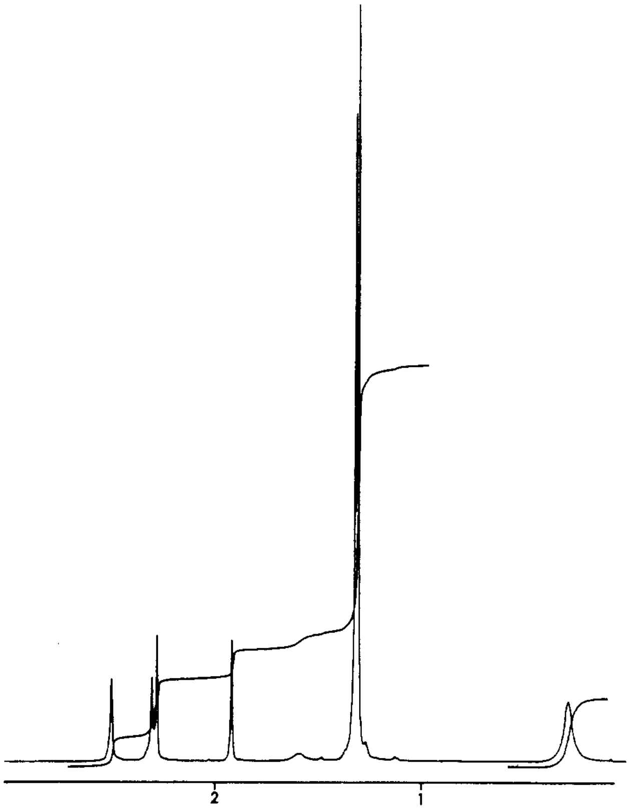

Figure 4. 360-MHz ^{1}H NMR spectrum, 0–3 ppm, of β-W(t-Bu$_2$Me$_2$dsp)$_2$ in CDCl$_3$ at 35 °C.

The signals due to the aromatic hydrogens of the W(t-Bu$_2$Me$_2$dsp)$_2$ complexes span a much wider range than that found for the free ligand, **1b**. Whereas the aromatic region of the free ligand is 7.40–6.95 ppm, the same hydrogens in the W(t-Bu$_2$Me$_2$dsp)$_2$ complexes span a range of 7.40 ppm to less than 6.00 ppm. If the aromatic region of the W(t-Bu$_2$Me$_2$dsp)$_2$ complexes were completely resolved, a 40-line spectrum would be observed. This prediction supposes that the chemical equivalence between the aromatic hydrogens on the left- and right-hand side of the parent ligand is lost on complexation. This 40-line spectrum

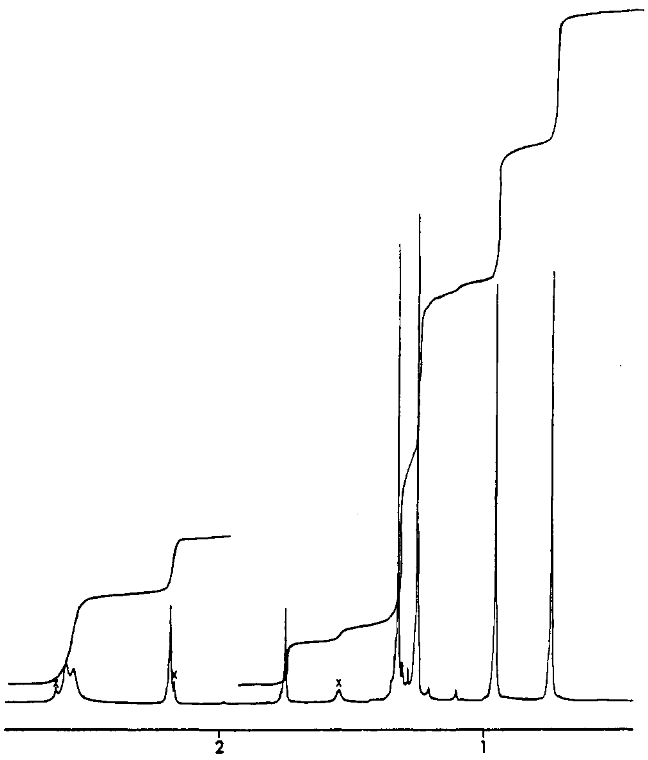

Figure 5. 360-MHz ^1H NMR spectrum, 0–3 ppm, of γ-W(t-$Bu_2Me_2dsp)_2$ in $CDCl_3$ at 35 °C (X = impurity).

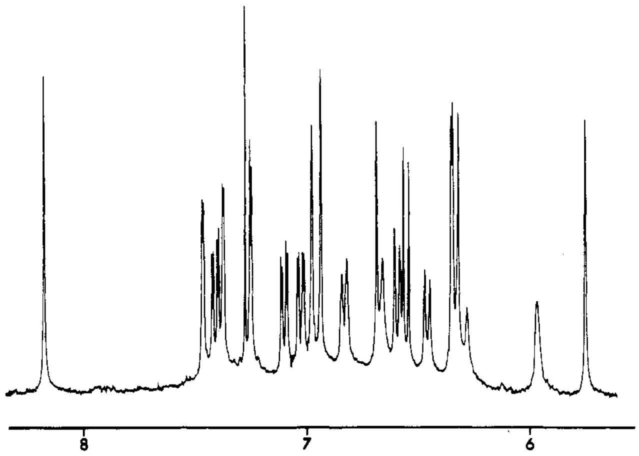

Figure 6. 360-MHz ^1H NMR spectrum, 6–8 ppm, of β-W(t-$Bu_2Me_2dsp)_2$ in $CDCl_3$ at 57 °C.

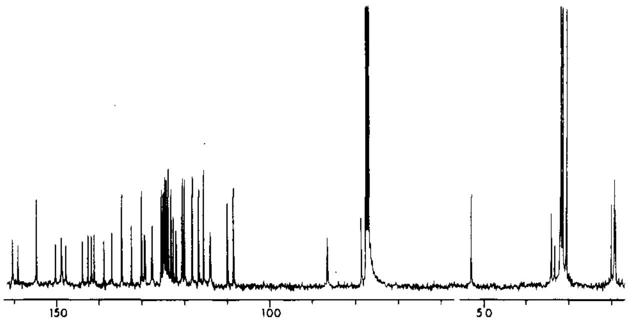

Figure 7. 90-MHz ^{13}C NMR spectrum of β-W(t-$Bu_2Me_2dsp)_2$ in $CDCl_3$ at 35 °C.

would consist of four H_a singlets, four H_b doublets, four sets of H_c doublet of doublets, and four H_d doublets, in addition to the four lines of the aldimine hydrogens. The aforementioned 40-line spectrum is not actually observed for any of the W(t-$Bu_2Me_2dsp)_2$ complexes. The peaks in the aromatic region are not completely resolved in any of the complex spectra. Nevertheless, it is clear that complexation does remove the chemical equivalence of the pairs of aromatic hydrogens that is observed in the parent ligand. See Figure 6. For each of the W(t-$Bu_2Me_2dsp)_2$ complexes at least three and in two cases all four sets of the H_c doublet of doublets are plainly visible. Those peaks in the aromatic region of the W(t-$Bu_2Me_2dsp)_2$ complex ^1H NMR spectrum that can be logically assigned as due to a H_a, H_b, H_c, H_d, or aldimine hydrogen are listed in Table V.

One unusual feature of the ^1H NMR spectrum of the W(t-$Bu_2Me_2dsp)_2$ complexes is the position of the aldimine hydrogen peaks. In the free ligand the chemical shift of the aldimine hydrogen is 8.62 ppm. In each of the W(t-$Bu_2Me_2dsp)_2$ complex spectra only one peak is observed downfield of the aromatic region. The other aldimine hydrogen signals appear to be buried in along with the aromatic hydrogens. In assigning these peaks and attempting to distinguish them from the signals due to the H_a hydrogens, we have assigned those singlets closest to the free ligand H_a value of 7.01 ppm as H_a hydrogens and the remainder of the singlets as aldimine hydrogens. No peaks logically assignable to a phenolic hydrogen are observed in the ^1H NMR spectrum of any of the W(t-$Bu_2Me_2dsp)_2$ complexes.

Only very preliminary variable-temperature ^1H NMR studies have been conducted thus far. The 360-MHz ^1H NMR spectrum of the β complex in $CDCl_3$ at 57 °C has been recorded. At this temperature, the *tert*-butyl signal at 0.28 ppm is still broad and the other *tert*-butyl signals remain bunched together around 1.30 ppm. There is a small change in the chemical shift values of the methyl signals and better resolution of the signals in the aromatic region of the spectrum, but otherwise the spectrum is unchanged.

Both the β and γ complexes have been heated continuously at 100 °C in Me_2SO-d_6, and their 35 °C 60-MHz ^1H NMR spectrum has been recorded intermittently. There is no perceptible change in the ^1H NMR spectrum of the β complex after 1 week. The γ complex begins to show signs of decomposition after only 3 days. There is no evidence that either sample underwent interconversion to a different stereoisomer under these conditions.

^{13}C NMR Spectra. The 90-MHz ^{13}C NMR spectrum of the free ligand, **1b**, in $CDCl_3$ consists of 13 peaks. Of these peaks, 10 fall within a range of 117–163 ppm and are attributed to the aldimine and aromatic carbons. Five of these 10 peaks give rise to doublets when the off-resonance proton-decoupled spectrum is recorded. This information, plus the principle of substituent additivity,[13] was used to assign the peaks present in this region of the ^{13}C NMR spectrum. See Table VI for chemical shift values and peak assignments. From these criteria, the peak at 163.05 ppm is assigned to the aldimine carbon. The remaining three peaks fall within the region of 19–34 ppm and are assigned to the methyl and *tert*-butyl carbons.

A 52-line ^{13}C NMR spectrum is anticipated for the W(t-$Bu_2Me_2dsp)_2$ complexes, assuming, as is indicated by the ^1H NMR spectra, that they possess no inherent symmetry. The 90-MHz ^{13}C NMR spectrum has been obtained for the β- and γ-W(t-$Bu_2Me_2dsp)_2$ complexes. See Table VI. The β complex in $CDCl_3$ gives rise to a 51-line spectrum. See Figure 7. Of these peaks, 37 fall within the range of 108–160 ppm and are attributed to the aldimine and aromatic carbons. Of these 37 peaks, 17 give rise to doublets and 20 remain as singlets when the off-resonance proton-decoupled spectrum is recorded. Of the remaining peaks, 11 fall within the range of 19–34 ppm and are assigned to the methyl and *tert*-butyl carbons. The three remaining peaks lie in a region devoid of peaks in the ^{13}C NMR spectrum of the free ligand. These peaks occur at 52.92, 78.44, and 86.38 ppm. The same three peaks are also present when the ^{13}C NMR spectrum of the β complex is recorded in Me_2SO-d_6. The off-resonance proton-decoupled spectrum of the β complex reveals these three peaks to be doublets.

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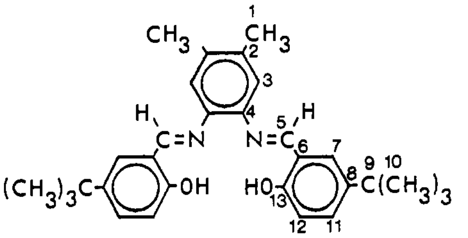
(13) (a) Inamoto, N.; Kushida, K.; Masuda, S.; Ohta, H.; Satoh, S.; Tamura, Y.; Tokumaru, K.; Tori, K.; Yoshida, M. *Tetrahedron. Lett.* **1974**, 3617. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley-Interscience: New York, 1981; Chapter 5.

Table VI. 90-MHz ^{13}C NMR Spectrum of the Free Ligand and β- and δ-W(t-$Bu_2Me_2dsp)_2$ Complexes in $CDCl_3$



free ligand (**1b**)		β-W(t-Bu_2-$Me_2dsp)_2$		γ-W(t-Bu_2-$Me_2dsp)_2$	
δ	assgnt[a]	δ	assgnt[b]	δ	assgnt
		18.97	1	19.26	1
		19.16		19.38	
19.46 q	1	19.22		19.72	
		19.99		19.95	
				29.75	
		30.44	10	31.01	10
31.42 q	10	31.32		31.38	
		31.73		31.55	
		31.79		31.79	
		33.22	9	32.43	9
33.96 s	9	33.87		33.62	
				33.97	
		34.05		34.05	
		52.92 d		52.88	
		78.44 d		73.85	
		86.38 d			
		108.32 d		108.63	
		109.76 d		110.26	
		113.84 d		113.45	
		115.46 d		116.42	
116.99 d	12	116.63 d		117.22	
		118.12 d		117.69	
		119.90 d		119.46	
120.57 d	3, 7 or 11	120.39 d		120.36	
		121.85 s		122.03	
		122.50 s		122.32	
		123.04 d		123.23	
		123.75 d		123.49	
		124.21 d		124.17	
		124.57 d		124.96	
		124.83 d		125.14	
		125.34 d		126.13	
		127.44 s		129.11	
128.43 d	3, 7 or 11	127.57 s		129.52	
		129.12 s		129.65	
		129.30 s		130.00	
130.41 d	3, 7 or 11	129.98 d		130.73	
		132.35 s		134.49	
135.99 s	2	134.57 d		135.43	
		136.86 s		138.04	
140.27 s	4 or 8	138.74 s		139.34	
141.37 s	4 or 8	141.07 s		140.44	
		141.75 s		141.81	
		142.52 s		141.94	
		143.87 s		142.53	
		147.76 s		147.47	
		148.70 s		149.75	
		148.88 s		150.82	
		150.27 s		152.21	
		154.62 d	5	154.36	
159.06 s	13	159.01 s		159.49	
		160.25 s		159.62	
163.05 d	5	160.35 s		160.05	

[a] Key: s = singlet, d = doublet, q = quartet. [b] Due to the close proximity of peaks for the methyl and *tert*-butyl carbons, the splitting in the off-resonance proton-decoupled spectrum could not be sorted out for these signals.

In attempting to assign the aldimine carbons of the β complex, we find only one peak, that at 154.62 ppm, that both has a chemical shift value near the free ligand value of 163.05 ppm and appears as a doublet in the ^{13}C off-resonance proton-decoupled spectrum. The three next closest doublets in the β-complex spectrum are at 134.57, 129.98, and 125.34 ppm. The missing or 52nd peak is assumed to be unresolved or to possess a chemical shift accidentally coincident with that of one of the other carbons. Since 12 peaks are expected for the methyl and *tert*-butyl carbons, but only 11 are observed, we presume the missing peak to belong to a methyl or *tert*-butyl carbon. More specifically, since only three peaks are observed for the quaternary carbon of the *tert*-butyl groups, the missing peak is presumably one of the signals from this carbon atom.

The ^{13}C NMR spectrum of the γ-W(t-$Bu_2Me_2dsp)_2$ complex is very similar to the spectrum found for the β complex. Again, 37 peaks are found in the range of 108–160 ppm. A total of 13 lines appear in the 19–34-ppm region. The unexpected 13th peak is presumably that at 29.75 ppm. Two additional peaks occur outside these two regions at 52.88 and 73.85 ppm. Strictly on the basis of relative intensities of the peaks, it appears that only one peak in the range of 160–135 ppm is due to a carbon atom that is not quaternary. This suggests, as is the case with the β complex, that only one of the four aldimine carbons in the γ complex has a chemical shift value that is near the value observed for the free ligand.

Attempted Oxidation of W(*t*-$Bu_2Me_2dsp)_2$ to W(*t*-$Bu_2Me_2dsp)_2^+$. An attempt to oxidize the β-W(t-$Bu_2Me_2dsp)_2$ complex to the corresponding tungsten(V) complex with Cl_2/CCl_4 appears to lead to a tungstate species instead. Treatment of β-W(t-$Bu_2Me_2dsp)_2$ as a suspension in Cl_2/CCl_4 produces only a minor color change. Although the maxima in the electronic spectrum of the product are shifted to higher energy, analysis of the product of this reaction reveals very low carbon, hydrogen, and nitrogen content. No further investigations were undertaken.

Side Products. Several other species have also been isolated from the product mixture besides the W(t-$Bu_2Me_2dsp)_2$ complexes. Table VII summarizes the chromatographic, analytical, and spectral data collected for these species.

The first of these three species, **2**, we believe to be a tungsten complex containing the parent ligand, **1b**, plus an organic fragment derived from the parent ligand. Three *tert*-butyl signals and two methyl signals are observed in the ^1H NMR spectrum of **2**. Also present in the ^1H NMR spectrum of **2** are pairs of H_b, H_c, and H_d signals attributable to the coordinated parent ligand. The four pairs of doublets centered around 4 ppm suggest the organic fragment may be partially reduced. Because of its high molecular weight and low volatility, a complete mass spectrum of this sample was not obtained. No further attempts were made to elucidate the structure of this species.

On the basis of the value of the mass spectral parent peak for **3** and the analytical results, we have assigned this product an empirical formula of $C_{19}H_{22}N_2O$. However, we do not yet know its molecular structure with exact certainty. This species appears to be a fragment of the parent ligand, **1b**, that has cyclized. The ^1H NMR spectrum of **3** reveals a single *tert*-butyl and a single methyl signal. The integration of these two peaks is 3 to 2, however, and not 3 to 1 as is observed for **1b**. This result suggests that **3** is derived from one *o*-phenylenediamine ring and one phenol ring. A H_b doublet, a H_c doublet of doublets, and a H_d doublet are also clearly visible in the ^1H NMR spectrum of **3**. The only other peak present in the ^1H NMR spectrum of **3** is buried in with the H_c signal. The 90-MHz ^{13}C NMR spectrum of **3** in Me_2SO-d_6 gives 13 peaks at 19.95, 31.33, 34.17, 111.50, 114.33, 116.45, 123.33, 128.84, 132.04, 134.47, 141.73, 150.32, and 155.74 ppm. The first three peaks can be assigned to the methyl carbons, the *tert*-butyl methyl carbons, and the quaternary *tert*-butyl carbon, respectively. Of the remaining 10 peaks, five appear to belong to quaternary carbons, on the basis of their relative intensities.

We have assigned an empirical formula of $C_{30}H_{38}N_2O_2$ to species **4**, again on the basis of spectral and analytical results. This species appears to be a reduced form of **1b** in which one of the aldimine groups is reduced to an amine. The ^1H NMR spectrum of **4** consists of two *tert*-butyl groups of equal intensity, two methyl groups of equal intensity, a methylene group, and two sets each of H_b, H_c, and H_d signals. The aldimine hydrogen expected at

Table VII. Chromatographic, Analytical, and Spectral Results for the Side Products

			anal.			360-MHz ^{1}H NMR[d]		
species	R_f	mp, °C	calcd[b]	found	m/e[c]	δ	J, Hz	assgnt[e]
2	0.60			C, 60.80		1.09 s (9)		*t*-Bu
				H, 6.34		1.20 s (9)		*t*-Bu
				N, 3.91		1.34 s (9)		*t*-Bu
						1.97 s (3)		Me
						2.16 s (3)		Me
						3.83 d (1)	13.0	
						3.94 d (1)	13.0	
						4.34 d (1)	13.0	
						4.51 d (1)	13.0	
						6.02 s (1)		
						6.03 s (1)		
						6.44 s (1)		
						6.48 d (1)	8.0	H_d
						6.73 d (1)	2.3	H_b
						6.82 d (1)	8.5	H_d
						6.98 s (1)		
						6.99 d (1)	2.6	H_b
						7.02 s (2)		
						7.05 d (1)	8.6	H_d
						7.14 dd (1)	2.3, 8.6	H_c
						7.16 d (1)	2.5	H_b
						7.41 dd (1)	2.2, 8.5	H_c
3	0.35	226-228	C, 77.52	C, 77.54	294 (34)	1.33 s (9)		*t*-Bu
			H, 7.52	H, 7.56	280 (21)	2.36 s (6)		Me
			N, 9.52	N, 9.48	279 (100)	7.04 d (1)	8.7	H_d
					140 (13)	7.36 dd (1)	2.4, 8.7	H_c
					125 (25)	7.37 s (1)		
					118 (34)	7.53 d (1)	2.4	H_b
					97 (12)			
					91 (10)			
					85 (16)			
					83 (13)			
					71 (25)			
					70 (11)			
					69 (17)			
					59 (12)			
					57 (42)			
					55 (22)			
4	0.15	199-200	C, 78.56	C, 77.92	458 (3)	1.00 s (9)		*t*-Bu
			H, 8.35	H, 8.17	457 (11)	1.07 s (9)		*t*-Bu
			N, 6.11	N, 5.71	456 (14)	2.35 s (3)		Me
					295 (17)	2.41 s (3)		Me
					294 (44)	5.53 s (2)		CH_2
					280 (22)	6.81 d (1)	8.4	H_d
					279 (100)	6.85 (1)	2.2	H_b
					147 (18)	7.05 d (1)	8.6	H_d
					91 (18)	7.09 s (1)		H_a
					77 (12)	7.20 d (1)	2.2, 8.3	H_c
					57 (12)	7.30 d (1)	2.2, 8.6	H_c
						7.35 d (1)	2.2	H_b
						7.59 s (1)		H_a or aldimine

[a] E. Merck Silica Gel 60 TLC plates, 0.25-mm thickness, were used; 2:1 v/v chloroform/hexanes was the eluent. [b] Calculated values based on the empirical formulas $C_{19}H_{22}N_2O$ and $C_{30}H_{38}N_2O_2$, respectively, for species **3** and **4**. [c] The m/e values are followed by relative intensities; parent peaks are 294 and 458, respectively, for species **3** and **4**. [d] Resonance signals reported in ppm downfield from tetramethylsilane. Key: s, singlet; d, doublet; dd, a doublet of doublets. Relative integrated intensities in parentheses. [e] H_a, H_b, H_c, and H_d assignments are referenced to the lettering scheme used for **1b**.

approximately 8.6 ppm either is not observed or is buried in with the aromatic signals. No signals logically assignable to a phenolic hydrogen or an amine hydrogen are observed, probably due to rapid exchange in $CDCl_3$.

Both **3** and **4** have been synthesized by the direct reduction of **1b** with trimethylamine–borane in acetic acid. The samples of **3** and **4** prepared by this method gave a ^{1}H NMR spectrum, mass spectrum, and a melting point identical with that of the corresponding samples of **3** and **4** isolated from the product mixture resulting from the reaction of tungsten hexacarbonyl and **1b**.

Discussion

Rigid Behavior. On the basis of the results of their analyses, the similarity in their electronic and infrared spectra, and the uniqueness of their R_f values and ^{1}H NMR spectra and on the supporting ^{13}C NMR studies, we have categorized the four isolated tungsten species as eight-coordinate bis(quadridentate Schiff base)tungsten(IV) complexes. The W(t-Bu$_2$Me$_2$dsp)$_2$ complexes appear to be diamagnetic, substitution inert, and, most importantly, stereoisomers of one another.

The synthesis and subsequent separation of the α-, β-, γ-, and δ-W(t-Bu$_2$Me$_2$dsp)$_2$ complexes constitutes several firsts. These complexes are the first examples of a group 6[32] metal forming an eight-coordinate complex with a pair of quadridentate ligands. In addition, we are not aware of any other case where this large a number of eight-coordinate stereoisomers have been detected for a single eight-coordinate complex. Nor have any of the eight-coordinate stereoisomers previously detected been rigid enough to isolate by conventional methods.

As has been previously discussed, the rigid character of early-transition-metal eight-coordinate complexes is a function of numerous variables. The energy of activation between two stereoisomers appears to increase and the rate of intramolecular rearrangement appears to decrease (1) on increasing the denticity of the ligand, (2) on changing from equivalent donor atoms to nonequivalent donor atoms, (3) on changing the electronic configuration of the metal from d^0 to d^2, and (4) on increasing the electron density about the metal as exemplified by the formation of cationic eight-coordinate complexes and those possessing third-row transition-metal ions vs. second or first. These trends have been deduced from a comparison of the results of the variable-temperature NMR studies summarized in Table I.

We attribute the rigid character displayed by the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes primarily to the nature of the ligand. In particular, the ligand is a quadridentate ligand with two distinctly different types of donor atoms, one a π acceptor (the imine nitrogen atoms) and the other a π donor (the phenolic oxygen atoms). The flexible nature of the Schiff-base ligand permits it to chelate in several different modes (vide infra). Yet having four tungsten-donor atom bonds anchored to one backbone undoubtedly reduces the number of pathways for intramolecular rearrangement and raises the energy barrier for those that might still remain. It is also important that these complexes are substitution inert, a consequence of the fact that tungsten(IV) is a d^2 metal ion and a third-row transition metal. The importance of the d-electron configuration of the metal in the stabilization of eight-coordinate stereoisomers is exemplified by a comparison of the results obtained in this study for the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes and the results obtained for the neutral bis(quadridentate Schiff base)zirconium(IV) complex, $Zr(dsp)_2$.[10] These complexes differ only in the d-electron configuration of the metal; yet, the former gives rise to stereoisomers and the latter does not.

Synthesis of the $W(t\text{-}Bu_2Me_2dsp)_2$ Complexes. *N,N'*-Bis(5-*tert*-butyl-2-hydroxybenzylidene)-1,2-diamino-4,5-dimethylbenzene (**1b**) was selected as a ligand over *N,N'*-disalicylidene-1,2-phenylenediamine (**1a**) for two reasons. First, the presence of the methyl and *tert*-butyl groups greatly enhances the solubility of the resulting complexes in organic solvents, which in turn simplifies the separation of these complexes from the remainder of the product mixture. Second, the presence of the methyl and *tert*-butyl groups also provides a convenient ^1H NMR handle by which to probe the stereochemistry of the resulting complexes. Their presence also simplifies the splitting in the aromatic region of the ^1H NMR spectrum relative to the spectrum of **1a**.

Oxidative decarbonylation of tungsten hexacarbonyl by the ligand has been used previously to prepare other tungsten(IV) eight-coordinate complexes including the tetrakis(8-quinolinolato)tungsten(IV) complexes[14], the tetrakis(picolinato)tungsten(IV) complexes,[15] and the tetrakis(2-mercaptopyrimidinato)tungsten(IV) complex[16]. Tris(picolinato)molybdenum(III)[15a] and tetrakis(picolinato)molybdenum(IV)[17] have also been prepared by this procedure using molybdenum hexacarbonyl. The preparation of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes extends this method to Schiff-base type ligands. No intermediate oxidation state tungsten species containing carbonyl ligands were isolated or detected in this reaction, which is consistent with previous observations.[14,15]

That the ligand is the oxidizing agent in this reaction is substantiated by the isolation of **4**, a reduced form of the parent ligand. In previous studies that relied on the oxidative decarbonylation of a metal carbonyl by the ligand to produce an eight-coordinate complex, oxidation by the ligand itself has been suggested but not necessarily substantiated. The 1,2,3,4-tetrahydro derivative of 8-quinolinol has been proposed to be the reduced form of 8-quinolinol produced when 8-quinolinol and tungsten hexacarbonyl are reacted together to produce the tetrakis(8-quinolinato)tungsten(IV) complex.[14,18]

Electronic and Infrared Spectra. Beside the high-energy bands at 36 900 and 29 200 cm^{-1}, which are also observed for the parent ligand, the electronic spectra of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are characterized by an intense band around 21 500 cm^{-1} and a much weaker shoulder near 15 700 cm^{-1}. By virtue of its intensity ($\epsilon > 10^4$), the high-energy band at 21 500 cm^{-1} is assigned as a charge-transfer band rather than as a d–d transition. More specifically, this charge-transfer band is assigned as a metal-to-ligand ($\pi^* \leftarrow d$) transition based on the analysis of the electronic spectra of the previously characterized eight-coordinate 8-quinolinolato[14,18] and picolinato tungsten(IV) and molybdenum(IV) complexes.[15b,17] The low-energy shoulder that is also present in all the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes is assigned as a d–d transition based, again, on the value of ϵ, which is 1 order of magnitude weaker than that of the other bands.

The infrared spectral shifts observed for the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are similar to those observed in other complexes containing the dsp^{2-} ligand. It has been previously noted[10,19] that the C═N stretch shifts very little on complexation from its free ligand value of approximately 1615 cm^{-1}. We find the shift to be less than 5 cm^{-1} for each of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes. It is also consistent with previous observations[19] that the phenolic C–O stretch is found to shift 25 cm^{-1} to a value greater than 1300 cm^{-1} on complexation.

NMR Spectra. Several explanations can be offered for why these complexes lack symmetry and thus give rise to the ^1H NMR spectra described above. We believe, however, when all the experimental evidence is combined and carefully scrutinized that only a single interpretation emerges that can be fully substantiated. We find results contradictory to all other lines of interpretation. The only explanation we find that experimental results fully support is that one or both of the $t\text{-}Bu_2Me_2dsp^{2-}$ ligands in each of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes is complexed to the tungsten(IV) center in a nonplanar fashion and that this distorts the backbone of the ligand enough to remove any symmetry the complex might otherwise possess.

An alternative explanation that should be examined, but for which we find contradictory results, is that at least one of the two quadridentate ligands complexed to the tungsten(IV) center is not the parent ligand, but a reduced form of it. Elemental analysis alone cannot be used to distinguish between this type of eight-coordinate tungsten(IV) complex and an authentic $W(t\text{-}Bu_2Me_2dsp)_2$ complex. The percent by weight values for these two species are too close to be useful in a case like this. Another reason for examining this possibility is that one of the other species recovered from the product mixture, beside the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes, was a reduced form of the parent ligand in which one of the two aldimine groups was reduced to an amine. This species, **4** could still conceivably function as a quadridentate ligand. Reduction is accompanied by elimination of the elements of symmetry present in the parent ligand. This is evident in the ^1H NMR spectrum of **4** that reveals two methyl and two *tert*-butyl signals. A complex containing **4** would therefore be expected to be a low-symmetry species.

Although the aromatic region of the ^1H NMR spectrum was not completely resolved for any of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes, we nonetheless find no direct evidence of peaks attributable to a secondary amine and a methylene group in the aforementioned spectra. These signals would be indicative of an aldimine group that had undergone reduction. Although the methylene signal in **4** occurs at 5.53 ppm and the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes also contain singlets in this region, the integration of these later peaks corresponds to one hydrogen and not to two hydrogens. Furthermore, although the peaks at 52.92 and 52.88 ppm in the ^{13}C NMR spectrum of the β and γ complexes, respectively, are within the chemical shift region generally found for a methylene carbon attached to a secondary aromatic amine,[20] the off-resonance

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proton-decoupled spectrum of the β complex does not support that assignment. A doublet is observed, not a triplet, as is required for a methylene carbon. Indeed, none of the carbons give rise to a triplet in the off-resonance proton-decoupled ^{13}C NMR spectrum of the β complex. The suggestion that some other reduced form of the parent ligand is present in these complexes cannot be substantiated either. The same splitting pattern present in the aromatic region of the parent ligand is reproduced in the ^1H NMR spectrum of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes. This would not be the case if one or more of the aromatic rings of the parent ligand had been reduced and resulting species were now functioning as a ligand.

The suggestion that the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are not really eight-coordinate in structure, but rather six- or seven-coordinate, is yet another possible explanation for the ^1H NMR spectra obtained for these complexes. In such six- or seven-coordinate species the parent ligand would presumably function as a bi- or more likely a tridentate ligand and possess at least one undissociated and uncoordinated phenolic group or an uncoordinated phenolate group or groups. There is no evidence in the ^1H NMR spectrum of any of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes for the presence of phenolic hydrogens. Although the evidence is indirect, neither magnetic susceptibility nor conductivity measurements have been performed; the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are most logically formulated as neutral, dimagnetic, and substitution-inert tungsten(IV) complexes. The nonshifted NMR spectra preclude paramagnetic complexes, and the TLC results on silica gel using chloroform as an eluent preclude charged complexes. The formulation of these complexes as neither six- or seven-coordinate complexes is consistent with these conclusions. A seven-coordinate $W(t\text{-}Bu_2Me_2dsp)_2$ complex containing a quadridentate and a tridentate ligand would have to possess a tungsten(III) center in order to be neutral. However, such a species would be paramagnetic and unlikely to give the kind of well-behaved ^1H NMR spectra actually observed. A six-coordinate $W(t\text{-}Bu_2Me_2dsp)_2$ complex containing tungsten(II) would also likely be paramagnetic. Neither it nor the seven-coordinate complex described above would be anticipated to show the air stability and substitution inertness that the actual $W(t\text{-}Bu_2Me_2dsp)_2$ complexes show. Finally, any tungsten(IV) six- or seven-coordinate species we can envision also fails to satisfy one or more of the conditions outlined above.

The most striking feature of the ^1H NMR spectrum of each of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes is the nonequivalence of the four *tert*-butyl groups. Other features of the ^1H NMR spectrum that the four $W(t\text{-}Bu_2Me_2dsp)_2$ complexes have in common are (1) three or four methyl signals, (2) one aldimine hydrogen peak within the 8.3–8.0 ppm range, (3) the remainder of the aldimine hydrogen signals shifted significantly upfield, (4) an aromatic region spanning a range approximately 1 ppm further upfield than that of the free ligand, (5) three or four clearly recognizable H_c doublet of doublets, (6) at least three distinguishable H_b doublets and/or H_d doublets, and (7) no detectable phenolic hydrogen signals. Furthermore, the ^1H NMR and ^{13}C NMR results obtained for the β and γ complexes are internally consistent. In all cases where groups of hydrogens show nonequivalence in the ^1H NMR spectrum the corresponding carbons to which these hydrogens are attached show nonequivalence in the ^{13}C NMR spectrum as well. This statement applies to the *tert*-butyl, methyl, aromatic, and aldimine groups.

Both the occurrence of four *tert*-butyl signals for each $W(t\text{-}Bu_2Me_2dsp)_2$ complex and the chemical shift range of these signals are somewhat unexpected. Relative to the free-ligand value of 1.30 ppm, shifts as large as 1 ppm upfield are found for the *tert*-butyl groups in the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes. See Table V. We have attributed the nonequivalence of the *tert*-butyl groups in the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes to the nonplanar bonding mode(s) of the $t\text{-}Bu_2Me_2dsp^{2-}$ ligand. We also attribute the upfield chemical shift values observed for some of the *tert*-butyl groups to the nonplanar bonding mode(s) of the $t\text{-}Bu_2Me_2dsp^{2-}$ ligand, plus the likelihood that some of the *tert*-butyl groups on one $t\text{-}Bu_2Me_2dsp^{2-}$ ligand are close enough to be shielded by the π-electron density of an aromatic ring on the other $t\text{-}Bu_2Me_2dsp^{2-}$ ligand. Ring current shifts of far greater than 1 ppm are common where a hydrogen or methyl group is situated above an aromatic ring.[21] All these results suggest that the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes possess structures devoid of any symmetry.

It is interesting to speculate as to the location of the four aldimine signals in the ^1H and ^{13}C NMR spectrum of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes. As previously noted, each of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes has one aldimine hydrogen with a chemical shift value of 8.1 ± 0.15 ppm or a value approximately 0.5 ppm upfield from the free-ligand value of 8.62 ppm. The other three aldimine hydrogens are assigned chemical shifts of 6.50 ppm or less. For the eight-coordinate zirconium(IV) complex, $Zr(dsp)_2$, in CD_2Cl_2 the aldimine hydrogens are reported as a sharp singlet at 8.50 ppm relative to the free-ligand value of 8.66 ppm.[10] We observe a slightly greater upfield shift for the aldimine hydrogen in the $Ni(t\text{-}Bu_2Me_2dsp)$ complex, which occurs at 8.40 ppm in $CDCl_3$.[22] However, in both the $Zr(dsp)_2$ complex and the $Ni(t\text{-}Bu_2Me_2dsp)$ complex the dsp^{2-} ligand chelates in a planar or nearly planar fashion—a situation unlikely in the case of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes. The situation is just as puzzling with regard to the aldimine carbons and the ^{13}C NMR spectra. The chemical shift of aldimine carbon of the free ligand, **1b**, is similar to the values reported for other Schiff-base compounds, e.g., *N*-benzylideneaniline where a value of 160.01 ppm has been reported.[13a] The ^{13}C NMR spectrum of the β and γ complexes contains only one signal each at 154.62 and 154.36 ppm, respectively, which is near the free-ligand value of 163.05 ppm, and can be attributed to the aldimine carbon. Again, the results obtained from the ^1H NMR and ^{13}C NMR spectra parallel one another.

Could it be that the three peaks in the ^{13}C NMR spectrum of the β complex at 52.92, 78.44, and 86.38 ppm are due to the other three aldimine carbon atoms? Distortion of the $t\text{-}Bu_2Me_2dsp^{2-}$ ligand to permit complexation would certainly result in distortion of some of the aldimine groups. The only other plausible assignment for these three peaks is as aromatic carbons that seem less likely to experience as large a distortion as the aldimine carbons. The assignment of these three peaks to the aldimine carbons is also consistent with the assignment of the aldimine hydrogens to the singlets as far upfield as 5.20 ppm in the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes.

As stated earlier, the singlets in the aromatic region of the ^1H NMR spectrum of the $W(t\text{-}Bu_2Me_2dsp)_2$ complexes are due to either the H_a or aldimine hydrogens. If the H_a hydrogens had been assigned to the singlets shifted upfield rather than the aldimine hydrogens, then the internal consistency between the ^1H NMR and ^{13}C NMR spectra alluded to earlier is lost. Ring currents could cause an upfield shift in the H_a hydrogens as is apparently observed for some of the *tert*-butyl signals. This assignment, however, leaves unexplained the apparent absence of aldimine carbon signals in the downfield region of the ^{13}C NMR spectrum of the β- and γ-$W(t\text{-}Bu_2Me_2dsp)_2$ complexes. If there is no dramatic shift in the aldimine hydrogen signals upon complexation, then there is no reason to expect a dramatic shift in the aldimine carbon signals upon complexation. Yet, only one aldimine carbon can be detected in the 135–160 ppm range of the ^{13}C NMR spectrum of these complexes. The aromatic ring carbons C-3, C-7, C-11, and C-12 (see Table VI) appear as doublets along with the aldimine carbon, C-5, in the ^{13}C off-resonance proton-decoupled NMR spectrum of the free ligand, **1b**. These four signals fall within the range of 117 to 130 ppm

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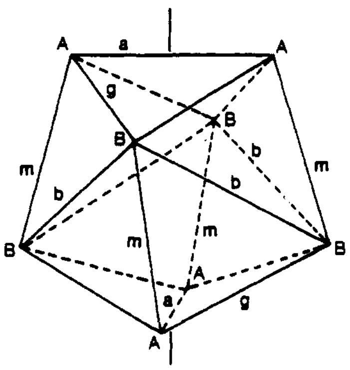

Figure 8. D_{2d} dodecahedron. The two sets of nonequivalent sites are labeled A and B. The four different edges are labeled $a(2)$, $b(4)$, $g(8)$, and $m(4)$ in accordance with the standard Hoard–Silverton nomenclature. See ref 2.

in the ^{13}C NMR spectrum of the free ligand. In the ^{13}C NMR spectrum of the β-W(t-$Bu_2Me_2dsp)_2$ complex the prerequisite 16 doublets of the four nonequivalent C-3, C-7, C-11, and C-12 carbons are observed in a range of 108–135 ppm. It therefore seems more appropriate to assign those signals shifted upfield in the ^1H NMR and ^{13}C NMR spectra of the W(t-$Bu_2Me_2dsp)_2$ complexes to the aldimine hydrogens and carbons than to the H_a hydrogens and the C-3 carbons.

Stereochemistry of the W(t-$Bu_2Me_2dsp)_2$ Complexes. Orgel's rule[23] has been a valuable guide to predicting the geometry and stereochemistry of eight-coordinate complexes. This approach is based on the consideration of the d-electron configuration of the metal and the π-donor/-acceptor properties of the donor atoms on the ligand. Orgel's rule[23] and its corollary[24] can be stated as follows: for complexes of the type MX_4Y_4 or $M(XY)_4$, where M = a d^1 or d^2 metal ion, ligands will orient themselves in a dodecahedral stereochemistry (see Figure 8) such that the A sites will be occupied by donor atoms with π-donor properties and the B sites will be occupied by donor atoms with π-acceptor properties. For d^0 complexes the reverse behavior is predicted; that is, the ligands are still predicted to orient themselves in a dodecahedral stereochemistry. However, the A sites will now be occupied by the π-acceptor groups and the B sites will be occupied by the π-donor groups. A recent analysis of this problem by Burdett, Hoffmann, and Fay[5] suggests that σ- and π-bonding effects along with steric effects must all be considered to explain the predictions encompassed by Orgel's rule and its corollary.

This rule has been experimentally substantiated. For example, the tetrakis(5-bromo-8-quinolinolato)tungsten(IV) complex[25] and its zirconium(IV) analogue, tetrakis(8-quinolinolato)zirconium(IV),[26] have both been structurally characterized and have been found to conform to Orgel's rule and its corollary, respectively. The 8-quinolinol ligands span the m edges in the $W(bq)_4$ complex, with the aromatic nitrogen donor atoms occupying the B sites and the phenolic oxygen donor atoms occupying the A sites. For the $Zr(q)_4$ complex, a d^0 metal ion eight-coordinate complex, the ligands span the g edges of the dodecahedron, with the oxygen donor atoms occupying the B sites and the nitrogen donor atoms occupying the A sites. The only cases where Orgel's rule or its corollary appears to be violated is when a d^1 metal ion is involved (the $VCl_4(diars)_2$,[27] $NbCl_4(diars)_2$,[28] and $TaCl_4(dmpe)_2$[29] complexes) or when the difference between the two types of atoms is small (O vs. S) as in the $Zr(Sacac)_4$[7b] and $Zr(OSCNMe_2)_4$[7f] complexes.

The W(t-$Bu_2Me_2dsp)_2$ complexes and the $Zr(dsp)_2$ complex constitute another pair of eight-coordinate complexes that differ only in the d-electron configuration of the metal. Since the dsp^{2-} ligand contains both π-acceptor groups and π-donor groups, it would be expected that these bis(quadridentate Schiff base) eight-coordinate complexes would also obey Orgel's rule and its corollary. The structure of the $Zr(dsp)_2$ complex[10] has been determined and has been found to obey the corollary to Orgel's rule for d^0 eight-coordinate complexes. The dsp^{2-} ligands in the $Zr(dsp)_2$ complex span the dodecahedral mam edges that place the oxygen donor atoms in the dodecahedral B sites and the nitrogen donor atoms in the dodecahedral A sites. Although the arrangement of the four oxygen and four nitrogen atoms conforms almost perfectly to the dimensions of the idealized dodecahedron, the backbone of the dsp^{2-} ligands was found to be skewed considerably from the two trapezoidal planes spanned by the donor atoms.

If the t-$Bu_2Me_2dsp^{2-}$ ligands were to wrap around the tungsten atom in such a way as to conform to Orgel's rule in the case of the W(t-$Bu_2Me_2dsp)_2$ complexes, the resulting dodecahedral complexes would have the oxygen donors occupying the A sites and the nitrogen donors occupying the B sites. This requires of necessity that a b edge be spanned by the t-$Bu_2Me_2dsp^{2-}$ ligand. The mbm, gbg, and gbm wrapping patterns would all place the donor atoms in the desired sites. However, since the b edge is the longest edge of the four dodecahedral edge types a, g, m, and b, the observed dodecahedral geometry would have to deviate significantly from the dimensions of the idealized dodecahedron. The two nitrogen donor atoms in the dsp^{2-} ligand form a five-membered chelate ring, while the two aldimine chelate rings formed by chelation through one nitrogen donor atom and the phenolic oxygen atom are six-membered chelate rings. The average length of the a edge in the $Zr(dsp)_2$ complex[10] is 2.670 Å. This value corresponds to the bite of the two nitrogen donor atoms in the dsp^{2-} ligand. The average length of the b edge in the $Zr(dsp)_2$ complex is 3.086 Å. For the $W(bq)_4$ complex[25] the average length of the b edge is 3.224 Å.

Of the wrapping patterns mentioned above that include a b edge, the mbm pattern appears the least plausible for steric reasons. None of these patterns, however, would permit the t-$Bu_2Me_2dsp^{2-}$ ligand to span the dodecahedral edges in a planar fashion. Since previously studied complexes containing the dsp^{2-} ligand reveal that the ligand can adopt a highly nonplanar wrapping pattern, none but the most highly strained wrapping patterns should be dropped from consideration for steric reasons alone. One example of the dsp^{2-} ligand adopting a highly nonplanar wrapping pattern is in the cobalt(III) complex, Co(dsp)(dbm), where dbm^- = dibenzoylmethanato.[30] The dsp^{2-} ligand in this complex adopts a β-cis type configuration. In this orientation one aldimine chelate ring occupies a cis position relative to the remainder of the chelating ligand.

If electronic effects are less important than steric constraints in the case of the W(t-$Bu_2Me_2dsp)_2$ complexes, then Orgel's rule might not be obeyed. Partial compliance to Orgel's rule would be achieved if the t-$Bu_2Me_2dsp^{2-}$ ligands spanned the gmg edges of the dodecahedron. Yet another wrapping pattern for the t-$Bu_2Me_2dsp^{2-}$ ligand is that achieved if three of the four edges of the square face of a square antiprism are spanned. This alternative stereochemistry would permit the dsp^{2-} ligand to chelate in a planar or nearly planar orientation. Once again, the resulting square antiprism would be expected to be distorted because the bite of the chelate rings varies from a six-membered ring to a five-membered ring back to a six-membered ring.

Until a single-crystal X-ray structure determination is performed on one or more of the W(t-$Bu_2Me_2dsp)_2$ complexes, the exact stereochemistry of these complexes will go unsolved. To date we have been unable to obtain suitable crystals of any of these complexes. However, the data at hand (IR, UV–visible, ^1H NMR, and ^{13}C NMR spectra and R_f values) do appear to support the

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following conclusions or observations. All the evidence points to W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes that contain *t*-Bu$_2$Me$_2$dsp^{2-} ligands chelating in a nonplanar fashion. To have a W(*t*-Bu$_2$Me$_2$dsp)$_2$ complex with no apparent symmetry requires that one and probably both *t*-Bu$_2$Me$_2$dsp^{2-} ligands are bonding in a nonplanar mode. How different the modes of wrapping vary from one complex to the next is difficult to assert. That the R_f values for the four complexes range from 0.92 to 0.29 suggests the backbone of the *t*-Bu$_2$Me$_2$dsp^{2-} ligands are oriented in quite different ways from one complex to the next.

In spite of the uniqueness of the ^{1}H NMR spectrum of each W(*t*-Bu$_2$Me$_2$dsp)$_2$ complex, the electronic spectra of the four W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes are nearly superimposable on one another. This suggests that the four nitrogen donor atoms and the four oxygen donor atoms may occupy similar sites in all four complexes. It is probable that the WN_4O_4 chromophore is similar in each complex but that the orientation of the remainder of the *t*-Bu$_2$Me$_2$dsp^{2-} ligands are skewed in a different fashion in each complex.

We find no special significance in the number of isomers isolated. In fact, there may be still other W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes present in the product mixture that were overlooked. The large number of isomers isolated, along with the nature of the ^{1}H NMR spectra obtained for the W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes would appear to rule out a dodecahedral complex containing *t*-Bu$_2$Me$_2$dsp^{2-} ligands spanning the *mam* edges as was found for the Zr(dsp)$_2$ complex. This stereochemistry is clearly favorable from the standpoint of steric considerations. That this stereochemistry appears not to be observed for the W(*t*-Bu$_2$Me$_2$dsp)$_2$ complex indicates that electronic effects are at least partially at play in determining the ultimate stereochemistry of the W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes.

Another piece of evidence that suggests that the *t*-Bu$_2$Me$_2$dsp^{2-} ligand is not spanning the *mam* edges in the W(*t*-Bu$_2$Me$_2$dsp)$_2$ complexes is the results obtained from mixed-ligand studies. Our attempts to synthesize a mixed-ligand eight-coordinate complex containing the *t*-Bu$_2$Me$_2$dsp^{2-} ligand and the bidentate ligand mpic$^-$, where mpic$^-$ = 5-methylpicolinato, have failed.[31] The mpic$^-$ ligand is believed to span the four *m* edges of the dodecahedron, with the nitrogen donors occupying the B sites and the oxygen donors occupying the A sites in the eight-coordinate complex tetrakis(5-methylpicolinato)tungsten(IV), W(mpic)$_4$.[15b] Assuming this is the case and assuming that the *t*-Bu$_2$Me$_2$dsp^{2-} ligand could span the *mam* edges, the W(*t*-Bu$_2$Me$_2$dsp)(mpic)$_2$ complex should exist. Since it does not, we conclude that two ligands are incompatible and that the *t*-Bu$_2$Me$_2$dsp^{2-} ligand will not span the *mam* edges when forming an eight-coordinate tungsten(IV) complex.

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Registry No. 1b, 94706-50-0; W(*t*-Bu$_2$Me$_2$dsp)$_2$, 94706-51-1; tungsten hexacarbonyl, 14040-11-0; trimethylamine–borane, 75-22-9; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; 5-*tert*-butyl-2-hydroxybenzaldehyde, 2725-53-3.

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(31) Unpublished results.

(32) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Contribution from the Departments of Chemistry and Biochemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804,
and Perkin-Elmer Corporation, Norwalk, Connecticut 06856

Square-Planar Cis- and Trans-C–Palladium(II) Complexes of N-Electron-Deficient Heteroaromatic Ligands.[1] Ligand Synthesis, Complexation, Spectral Analyses, and Complex Interaction with Phage PM2 DNA[+]

GEORGE R. NEWKOME,[*,†] WALLACE E. PUCKETT,[†] GARRY E. KIEFER,[†] VINOD K. GUPTA,[†]
FRANK R. FRONCZEK,[†] DANIEL C. PANTALEO,[†,2] GREGORY L. McCLURE,[‡] JANELL B. SIMPSON,[§]
and WALTER A. DEUTSCH[§]

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A new class of organometallic Pd(II) complexes has been synthesized utilizing functionalized bipyridine or phenanthroline ligands that are capable of forming intramolecular cis bis anionic carbon to metal bonds. The ^{1}H and ^{13}C NMR spectra for the ligands and related complexes are reported. The tetradentate bipyridine ligand undergoes facile complexation with Pd(II) salts to give the complex possessing two C–Pd bonds, whereas the corresponding phenanthroline analogue is capable of forming only a single C–Pd bond. Single-crystal X-ray structure analyses have revealed that angular distortions are responsible for these reactivity differences. ^{13}C NMR and IR spectra of these complexes and the related pyridine and pyrazine complexes having trans-C–metal bonds are also presented. Details of the spectral assignments are given, and the ^{13}C NMR chemical shifts are interpreted in terms of the strain and/or electronic effects. The stereochemistry of the chelate ring was found to be the most important factor in determining the chemical shifts. The binding of *cis*-organopalladium complexes to phage PM2 DNA is reported where increased binding is correlated with the presence of cis-C–Pd bonds.

Introduction

There has been considerable attention focused on the study of palladium complexes in organic synthesis,[3] catalytic processes,[4] chemical reactivity,[5,6] spectroscopy,[7,8] and structural aspects.[9] Recently, new classes of stable organopalladium(II) complexes, which possess both intramolecular C- and N-coordination,[10–12] have been prepared. The increasing importance of such cycloorganometallic complexes has led us to investigate cyclic complexes

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[†] Department of Chemistry, Louisiana State University.

[‡] Perkin-Elmer Corp.

[§] Department of Biochemistry, Louisiana State University.

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