Inorg. Chem. **1994**, *33*, 187–191

Articles

Correlation among Alkoxide→Tungsten π-Bonding, Spin State, and Reactivity in $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$

Helmut Rothfuss, John C. Huffman, and Kenneth G. Caulton*

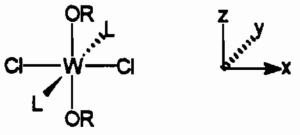
Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405

Received June 3, 1993[⊛]

The reaction of $WCl_4(PMe_2Ph)_2$ with 2 equiv of $TlOCH_2CF_3$ gives $W(OR_f)_2Cl_2(PMe_2Ph)_2$, which is shown by solution spectroscopic and solid-state (X-ray diffraction) methods to have a *trans,cis,cis* stereochemistry. The resulting ligand field leaves the two d electrons spin-paired in a single orbital, which enhances O→W π-donation and tends to increase the metal valence electron count to (or near) 18. The electron configuration leaves the molecule surprisingly unreactive toward PMe_2Ph, H_2, H_2O, and even O_2. The W–O bonds are short (1.844(5) and 1.852(5) Å), the W–Cl bonds are long (2.4865(19) and 2.4772(19) Å), and the W–O–C angles are large (142.2(5) and 144.8(5)°). A d-orbital splitting diagram and the structural evidence for significant O→W π-bonding is used to rationalize some aspects of structure (e.g., W–Cl bond lengths), as well as the eclipsing of the two W–O–C planes. Crystallographic data (–173 °C): a = 9.583(2) Å, b = 14.277(3) Å, c = 19.287(4) Å, and β = 102.66(1)° with Z = 4 in space group $P2_1/c$.

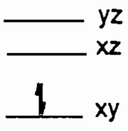
Introduction

It has been reported[1] that d^2 W(IV) species of structure **I** can exist in two distinct magnetic forms, spin-singlet or spin-triplet, depending on the identity of the group R. Such "spin isomers" have been compared to "high-spin" and "low-spin" forms of rigorously octahedral MX_6 species of configuration d^4–d^7, except that the spin isomers of **I** involve only the distribution of electrons among the now-nondegenerate orbitals derived from the t_{2g} subset of the five d orbitals. For species **I**, the low-spin form has been documented for OR = $O(C_6H_4X)$ where X = Me, Br, and Ph. The high-spin form is established for the very bulky $O(2,6\text{-}Ph_2C_6H_3)$.[2] The applicable splitting diagrams are **A** for the para-substituted phenoxy species and **B** for the $O(2,6\text{-}Ph_2C_6H_3)$ case.

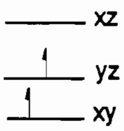


L = PMe_2Ph or $PMePh_2$

I



A



B

The former represents strong bonding (W–O = 1.844(5) Å), and the latter, weak bonding (W–O = 1.966(4) Å). Such differences are attributed to O→W π-bonding.

We have been interested in structural and reactivity manifestations of such O→M π-donation,[3] and we report here our results for an aliphatic alkoxide analog of the two reported aryloxide cases.

Experimental Section

General Details. All manipulations under ambient conditions (25 °C, 1 atm) were carried out in a glovebox under an argon atmosphere. The glassware was rigorously flame-dried; NMR tubes were kept at 110 °C in an oven. Aromatic solvents were dried over alkali metal, and CD_2Cl_2 was dried over P_4O_{10}; all solvents were freshly distilled before use. NMR spectra were recorded on a Bruker AM 500 and a Nicolet NT 360 spectrometer. The phosphorus chemical shift is reported using 85% H_3PO_4 as external standard, a negative chemical shift being upfield. Infrared data were obtained from a KBr pellet on a Nicolet 510P FT-IR instrument.

Synthesis of $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$. A 279.2-mg sample of $WCl_4(PMe_2Ph)_2$ (0.464 mmol) was dissolved in 20 mL of toluene, and 281.5 mg of $TlOCH_2CF_3$ (0.928 mmol) in 5 mL of toluene was slowly added. There was immediate precipitation of white thallium chloride. The color of the solution turned slowly from bright orange to pale yellow and then (after additional stirring for 8 h) to green-brown. The precipitate was allowed to settle, the solution was filtered over Celite, and the solvent was removed under vacuum. The residue was dissolved in 4 mL of toluene to give a dark brown-green solution. After the volume was reduced to 2 mL, the solution was kept at –20 °C for 3 days. Green crystals containing some brown $WOCl_2(PMe_2Ph)_3$ were formed. The volume of the mother liquor was reduced to 1 mL and the sample was again kept at –20 °C, resulting in more green crystals. The crystals were combined and recrystallized in 1 mL of toluene at –20 °C to give pure green crystals of $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$. Yield: 35%.

^1H NMR (500 MHz, CD_2DCl_2, 25 °C): δ 1.56 (d, $^2J_{HP}$ = 9.6 Hz, 12H, PCH_3), 3.83 (q, $^3J_{HF}$ = 9.0 Hz, 4H, CH_2CF_3), 7.20–7.24 (m, 4H, Ph), 7.36–7.42 (m, 6H, Ph). $^{31}P\{^1H\}$ NMR (146.2 MHz, C_6D_6, 25 °C): δ –130.3 (s, $^1J_{PW}$ = 395.2 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C): δ 23.4 (d, $^1J_{CP}$ = 30.9 Hz, PCH_3), 93.8 (q, $^2J_{CF}$ = 37.0 Hz, CH_2CF_3), 124.0 (q, $^1J_{CF}$ = 179.1 Hz, CH_2CF_3), 128.9 (d, J_{CP} = 9.1 Hz, Ph), 130.0 (d, J_{CP} = 9.1 Hz, Ph), 130.3 (s, para), 155.7 (d, $^1J_{CP}$ = 45.7 Hz, ipso). IR (ν, cm^{-1}) for the 950–1300-cm^{-1} region (ν(C–O) and ν(C–F)): 951 (s), 1080 (sh), 1119 (vs), 1159 (s), 1173 (s), 1273 (s), 1291 (sh).

[⊛] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

(1) Atagi, L. M.; Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 439. Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413.

(2) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1989**, *28*, 780.

(3) Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837. Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725. Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

0020-1669/94/1333-0187$04.50/0

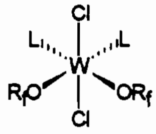
Table 1. Crystallographic Data for $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$

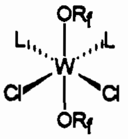
formula	$C_{20}H_{26}Cl_2F_6O_2P_2W$	space group	$P2_1/c$
a, Å	9.583(2)	T, °C	−173
b, Å	14.277(3)	λ, Å	0.710 69
c, Å	19.287(4)	ρ_{calcd}, g cm^{-3}	1.881
β, deg	102.66(1)	μ(Mo Kα), cm^{-1}	49.7
V, Å^3	2574.49	R	0.0299
Z	4	R_w	0.0331
fw	729.12		

Structure Determination of $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$. A small parallelepiped was cleaved from a crystal of dimensions 2 mm × 2 mm × 1.5 mm and affixed to a glass fiber using silicone grease. The mounted sample was then transferred to a goniostat, where it was cooled to −173 °C for characterization and data collection. All manipulations were performed using inert-gas handling techniques (N_2 gas). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to the unique space group $P2_1/c$. Subsequent solution and refinement confirmed this choice. Data were collected ($6° < 2\theta < 45°$) using a standard moving-crystal/moving-detector scan with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects and absorption. Equivalent data were then averaged to yield a unique set of intensities (Table 1). The structure was solved by direct methods (SHELXS) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier map and were included in the final cycles of refinement. A final difference Fourier map was featureless, the largest peak being 1.2 e/Å^3 at the W site, with all other peaks less than 0.7 e/Å^3. The largest negative intensity was −0.6 e/Å^3. The results of the structure determination are shown in Tables 2 and 3 and Figures 1 and 2.

Results

Synthesis and Characterization. Reaction of WCl_4L_2 (L = PMe_2Ph) with $TlOR_f$ (W:Tl = 1:2) in toluene gives immediate precipitation of thallium chloride, and the color of the solution changes slowly from bright orange to pale green-brown. Recrystallization from toluene gives green crystals of $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$, whose phosphorus nuclei are equivalent and whose four OCH_2 hydrogens are equivalent. One P*Me* ^{1}H NMR doublet rules out any structure based on *trans* phosphines but leaves the following structures as possible:





Structure. (a) Solid State. Single-crystal X-ray diffraction was used to determine the structure at −173 °C. The molecule adopts a structure very close to the octahedral shape (Figure 1), with *cis* angles within 8° of 90° and *trans* angles within 6° of 180°. The observed isomer has chlorides *cis*, phosphines *cis*, and alkoxides *trans*. *Cis* phosphines might be considered as surprising, considering the mutual repulsion between two such groups, but the *doublet* character of the P–CH_3 ^{1}H NMR signals suggests mutual *cis* disposition of the phosphines (i.e., no virtual coupling, consistent with $^2J_{PP} < 15$ Hz), even in solution. The actual symmetry of the molecule (ignoring phosphine substituents) is approximately C_{2v}, and both alkoxide OCC planes lie nearly in the idealized mirror plane (Figure 2). That is, they bisect the P–W–P and Cl–W–Cl angles. The W–O–C angles are very similar (142.2(5) and 144.8(5)°), and both CH_2CF_3 groups adopt the same conformation; one of these groups directs the oxygen $\pi(\|)$ lone pairs *away* from the chlorine lone pairs and toward the hydrocarbon environment. This latter would appear to be the underlying cause of this rotational conformation.

The two W-Cl bond lengths are chemically equivalent, as are the two W–P distances. In fact, these *four* distances are all essentially 2.48 Å. The Cl–W–Cl angle is somewhat compressed (86.5(1)°). The W–O distances, ~1.85 Å, are much shorter than single bonds (*vide infra*).

(b) Solution. In order to exclude the possibility that packing forces control the stereochemistry of $W(OR_f)_2Cl_2L_2$ found in the solid state, solution NMR studies were carried out. Crystals of $W(OR_f)_2Cl_2L_2$ were dissolved at −80 °C in CD_2Cl_2, and the solution was quickly placed in an NMR probe precooled to −80 °C. Both ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at this temperature and at 20 °C increments up to +20 °C.[4] At all temperatures, the spectra were essentially those of the material studied by dissolving solid at +20 °C. In particular, the ^{1}H NMR doublet for the P*Me* group (i.e., the lack of a virtual triplet) shows that the phosphines are *cis*, and remain so. Finally, a spectrum of this same solution was recorded again at −80 °C. This duplicates the first low-temperature spectrum and confirms that the temperature cycle did not cause any isomerization.

A test for thermal population of a paramagnetic form of $W(OR_f)_2Cl_2L_2$ was made by ^{1}H and ^{31}P NMR spectroscopy at high temperature in toluene-d_8. No evidence for paramagnetic effects (i.e., line broadening or chemical shift alteration) was observed at +60 °C.[5]

Reactivity. $W(OR_f)_2Cl_2L_2$ shows no reaction with a 10-fold excess of free PMe_2Ph after 24 h. Similarly, there is neither a color change nor a change in the ^{1}H and ^{31}P{^{1}H} NMR spectra of $W(OR_f)_2Cl_2L_2$ under excess H_2 (1 atm) after 1 day in toluene-d_8. Surprisingly, there is neither net reaction within 24 h at 25 °C nor even NMR spectroscopic evidence for any chemical shift change for $W(OR_f)_2Cl_2L_2$ in the presence of excess H_2O in CD_2Cl_2. From −60 up to +20 °C, there is no observable change in line width for the H_2O signal in the ^{1}H NMR spectrum of a sample of $W(OR_f)_2Cl_2L_2$ in water-saturated CD_2Cl_2. This indicates that even hydrogen bonding does not occur between the water molecules and the alkoxide ligands. In an additional attempt, O_2 was bubbled for 10 min through a solution of $W(OR_f)_2Cl_2L_2$ in CD_2Cl_2. Visually, as well as by NMR spectroscopy (^{1}H and ^{31}P{^{1}H} NMR assay), the sample showed no signs of decomposition. Even after 24 h, 50% of $W(OR_f)_2Cl_2L_2$ remained in a tube sealed under 1 atm of O_2.

Discussion

The results in hand raise several questions: (1) Why are the phosphines *cis* and the chlorides *cis* in $W(OR_f)_2Cl_2L_2$, given that they are *trans* in both **IA** and **IB**? (2) Why are the two W–O–C groups coplanar, since this forces the oxygen lone pairs to compete for the same tungsten d_π orbital? (3) Why are the alkoxide ligands mutually *trans* in all three $W(OR)_2Cl_2L_2$ compounds characterized to date?

We will address these questions after some general discussion about the results reported here.

Bonding and Structural Implications. The synthesis and characterization of a new example of the $W(OR)_2Cl_2L_2$ molecular class permit a number of conclusions. A *cis* phosphine stereochemistry in this product is surprising, since the phosphines are *trans* in the reagent complex WCl_4L_2. The fact that the phosphines (in contast to **IA** and **IB**) are *cis* and the chlorides are *cis*, yet $W(OR_f)_2Cl_2L_2$ fits the previously established[1] structure/magnetism correlation, establishes that the P/Cl stereochemistry is not of central importance to this effect.

The example of $W(OR_f)_2Cl_2(PMe_2Ph)_2$ confirms that low-spin (diamagnetic) behavior correlates with short W–O bonds. Appropriate comparison compounds for a W^{IV}–O single bond show much longer bond lengths. In $W(H)_3(OPh)(PMe_3)_4$[6] and

---

(4) Over the 100 °C temperature range, the P*Me* ^{1}H NMR chemical shift shows no detectable temperature dependence. The CH_2 signal of the fluoroalkoxide shifts by less than 0.3 ppm.

(5) By 75 °C, decomposition to a black precipitate and some $WOCl_2L_3$ and CF_3CH_2OH became rapid.

(6) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1204.

Table 2. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$

	x	y	z	$10B_{iso}$, Å^2		x	y	z	$10B_{iso}$, Å^2
W(1)	3114.8(2)	538.4(2)	2587.0(2)	10	H(4)	−20(6)	25(5)	152(5)	37(15)
P(2)	1348(1)	838(1)	2200(1)	14	H(5)	67(6)	−28(5)	135(6)	44(15)
C(3)	996(6)	1534(5)	1194(6)	22	H(6)	39(5)	−34(5)	232(5)	30(13)
C(4)	452(6)	31(5)	1783(6)	21	H(7)	117(4)	27(4)	412(4)	8(9)
C(5)	738(5)	1256(4)	3140(5)	17	H(8)	38(5)	91(5)	524(5)	35(14)
C(6)	792(6)	833(6)	3990(5)	25	H(9)	−39(7)	205(6)	505(6)	65(19)
C(7)	370(6)	1146(7)	4734(6)	31	H(10)	−47(6)	281(5)	369(6)	47(15)
C(8)	−104(6)	1885(7)	4632(7)	39	H(11)	19(6)	236(5)	249(6)	40(14)
C(9)	−161(6)	2307(6)	3802(7)	34	H(12)	358(5)	221(4)	500(4)	16(11)
C(10)	240(6)	1990(5)	3054(6)	24	H(13)	273(6)	163(5)	483(5)	34(13)
P(11)	3504(1)	1793(1)	3466(1)	12	H(14)	382(5)	131(4)	502(4)	14(10)
C(12)	3396(6)	1736(5)	4724(5)	20	H(15)	516(5)	191(4)	397(5)	27(12)
C(13)	4744(6)	2237(5)	3600(5)	18	H(16)	491(6)	240(5)	299(6)	50(15)
C(14)	2798(5)	2703(4)	3075(5)	13	H(17)	472(5)	274(5)	399(5)	36(13)
C(15)	2165(5)	3077(5)	3598(5)	16	H(18)	207(5)	291(4)	417(5)	34(13)
C(16)	1620(5)	3757(5)	3274(5)	18	H(19)	122(4)	399(4)	363(4)	2(9)
C(17)	1733(5)	4090(5)	2413(6)	19	H(20)	132(5)	450(4)	217(4)	12(9)
C(18)	2362(6)	3751(5)	1874(5)	18	H(21)	250(6)	397(5)	127(6)	48(16)
C(19)	2877(6)	3056(4)	2200(5)	15	H(22)	320(6)	283(5)	183(5)	33(13)
P(20)	4731(1)	482(1)	2037(1)	13	H(23)	514(5)	−83(4)	186(5)	17(12)
C(21)	5118(6)	−427(5)	1444(5)	20	H(24)	458(6)	−62(5)	91(6)	37(14)
C(22)	4817(6)	1214(5)	1089(5)	18	H(25)	565(5)	−35(4)	115(4)	11(10)
C(23)	5893(5)	649(4)	2880(5)	13	H(26)	533(6)	115(5)	84(6)	46(17)
C(24)	5993(5)	335(4)	3796(5)	17	H(27)	432(5)	124(4)	62(5)	17(11)
C(25)	6863(5)	412(4)	4430(5)	15	H(28)	478(5)	175(5)	138(5)	34(14)
C(26)	7652(5)	830(5)	4174(5)	18	H(29)	549(5)	7(4)	401(5)	21(11)
C(27)	7552(5)	1134(5)	3266(5)	18	H(30)	698(6)	18(5)	500(6)	43(14)
C(28)	6691(5)	1051(4)	2636(5)	15	H(31)	823(6)	90(5)	465(6)	44(14)
P(29)	2983(1)	−935(1)	2742(1)	14	H(32)	804(5)	142(4)	311(4)	10(9)
C(30)	4012(6)	−1590(5)	3254(6)	23	H(33)	665(5)	121(4)	203(5)	16(11)
C(31)	1997(6)	−1495(5)	3183(6)	23	H(34)	390(5)	−209(5)	303(5)	21(11)
C(32)	2743(5)	−994(4)	1465(5)	14	H(35)	463(6)	−144(4)	309(5)	28(12)
C(33)	2564(5)	−1614(5)	799(5)	19	H(36)	406(5)	−160(5)	388(6)	35(13)
C(34)	2372(6)	−1414(5)	−172(6)	21	H(37)	138(6)	−128(5)	295(6)	41(14)
C(35)	2354(5)	−599(5)	−432(5)	18	H(38)	211(5)	−207(5)	300(5)	31(13)
C(36)	2550(5)	11(4)	246(5)	14	H(39)	211(5)	−146(5)	378(6)	34(13)
C(37)	2733(5)	−173(4)	1217(5)	14	H(40)	252(4)	−215(4)	103(4)	4(9)
H(1)	125(4)	206(4)	139(4)	14(10)	H(41)	219(6)	−182(5)	−67(6)	57(17)
H(2)	128(5)	138(4)	65(5)	32(13)	H(42)	223(7)	−51(6)	−103(7)	72(20)
H(3)	31(6)	159(4)	110(5)	28(12)	H(43)	251(4)	52(4)	3(4)	14(10)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$

W(1)–Cl(2)	2.4865(19)	F(8)–C(6)	1.336(8)
W(1)–Cl(3)	2.4772(19)	F(9)–C(6)	1.336(8)
W(1)–P(16)	2.4892(19)	F(13)–C(12)	1.321(9)
W(1)–P(25)	2.4810(20)	F(14)–C(12)	1.356(9)
W(1)–O(4)	1.844(5)	F(15)–C(12)	1.324(9)
W(1)–O(10)	1.852(5)	O(4)–C(5)	1.406(9)
F(7)–C(6)	1.343(9)	O(10)–C(11)	1.401(8)
Cl(2)–W(1)–Cl(3)	86.51(6)	P(16)–W(1)–O(4)	92.13(16)
Cl(2)–W(1)–P(16)	87.52(6)	P(16)–W(1)–O(10)	89.24(15)
Cl(2)–W(1)–P(25)	173.68(6)	P(25)–W(1)–O(4)	90.13(15)
Cl(2)–W(1)–O(4)	87.92(15)	P(25)–W(1)–O(10)	93.22(15)
Cl(2)–W(1)–O(10)	88.54(15)	O(4)–W(1)–O(10)	176.15(20)
Cl(3)–W(1)–P(16)	173.93(6)	W(1)–O(4)–C(5)	142.2(5)
Cl(3)–W(1)–P(25)	87.43(6)	W(1)–O(10)–C(11)	144.8(5)
Cl(3)–W(1)–O(4)	88.77(16)	O(4)–C(5)–C(6)	109.5(6)
Cl(3)–W(1)–O(10)	89.49(15)	O(10)–C(11)–C(12)	109.5(6)
P(16)–W(1)–P(25)	98.57(6)		

$W(H)_3(\eta^1\text{-}O_2CEt)(PMe_3)_4$,[7] the distances are 2.13 and 2.18 Å, respectively. Note that these are much longer than the W–O distance in **IB** (1.97 Å), which indicates that the O-2,6-$Ph_2C_6H_3$ ligand participates in *more* O→W π-bonding than available simply from d_{xz}.[8] That is, some π-donation is possible even into a singly-occupied d_π orbital.[9]

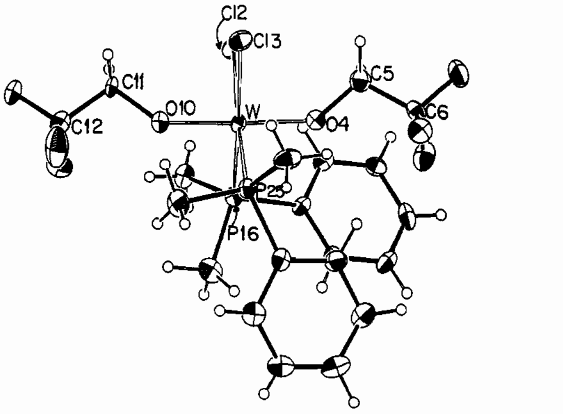


Figure 1. Stereo ORTEP drawing of $W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2$ viewed edge-on to the WCl_2P_2 plane showing the similar bending of the two W–O–C angles.

If the existence of W–O multiple bonding depends upon displacing one electron from a d_π orbital into the d_{xy} orbital, it follows that ligands affected by the population of the d_{xy} orbital should also show alterations in the lengths of their bonds to tungsten. The ligands most sensitive to this effect will be those

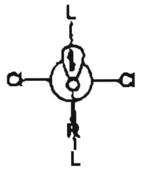
---

(7) Alvarez, R.; Carmona, E.; Galindo, A.; Gutiérrez, E.; Marin, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. *Organometallics* **1989**, *8*, 2430.

(8) As metal oxidation state (and electron deficiency) increases, even the bulky O-2,6-$Ph_2C_6H_3$ ligand can show enhanced π-donation.[2] In W(O-2,6-$Ph_2C_6H_3)_2Cl_3(PMe_2Ph)$, the W–O distances are 1.85 and 1.88 Å (i.e., comparable to those in **1** and **IA**).

bearing lone pairs. This prediction is strongly confirmed, in that the W–Cl distances are 2.35, 2.46, and 2.48 Å in **IB**, **IA**, and $W(OR_f)_2Cl_2(PMe_2Ph)_2$, respectively. The W–Cl bonds lengthen in the low-spin molecules due to enhanced filled–filled repulsions between the d_{xy}^2 and chloride lone pairs. The W–Cl distances in $W(OR_f)_2Cl_2L_2$ and **IA** are comparable to those (single) bonds in *trans*-WCl_2L_4 (L = PMe_3[10] at 2.43 Å and PMe_2Ph[11] at 2.45 Å). This conclusion concerning W–Cl bond lengths serves as a remainder that chloride must also be recognized[3] as a potential π-donor ligand when suitable metal orbitals are not all doubly-occupied. While chloride is established[3] to be a weak donor than a conventional alkoxide, when the OR ligand donor power is suppressed (as in O-2,6-$Ph_2C_6H_3$) by any combination of electronic and steric effects, then Cl→M π-donation can be effective in the high-spin state. This effect will therefore enhance the change in W–Cl bond length between, e.g., **IA** and **IB**. It is not simply the comparison of a "pure" W–Cl σ-bond "suffering" filled–filled repulsions in **IB**. The d_{xz} and (to a lesser extent) d_{xy} orbitals in **IB** allow some degree of Cl→W π-donation in that class of molecules, thus increasing the W–Cl bond length difference.

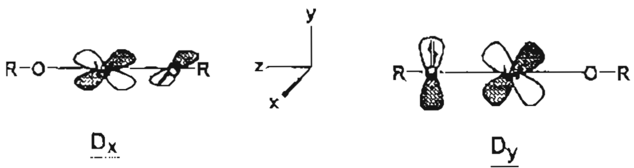
The previously unobserved *cis,cis* stereochemistry of the phosphines and chlorides, respectively, in $W(OR_f)_2Cl_2L_2$ puzzled us. With the structure in hand, we feel that the rotational conformation about the W–O bonds offers some explanation. If the chlorines (with their lone pairs) are accepted as a center of accumulation of negative charge, the *cis* WCl_2 isomer is unique in spatially concentrating that negative charge so that both OR_f groups can direct their $\pi(\parallel)$ orbitals into the hydrocarbon region of the phosphine substituents. While this gives a 135–180° dihedral angle between $\pi(\parallel)$ and the chlorine region, the *trans* WCl_2 isomer (**II**) permits at most a 90° angle.



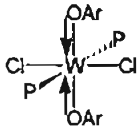
II

What has not been adequately addressed to date is the correlation of the torsional angle between the two W–O–C planes and the orthogonal character of the two empty d_π orbitals in A. In $W(OC_6H_4Me)_2Cl_2(PMePh_2)_2$, the aryloxy ring planes are nearly coplanar, which eclipses the oxygen lone pairs in a manner that at first appears counterproductive to the formation of one π-bond by each OAr ligand (**C**). However, since the W–O–C(ipso) angles (166.3 and 171.7°) in **IA** are nearly linear, the oxygen lone pairs become more nearly degenerate,[12] and thus two orthogonal lone pairs can donate ($\mathbf{D}_x$ and $\mathbf{D}_y$), giving an 18-valence electron count (**III**). For $W(OR_f)_2Cl_2(PMe_2Ph)_2$, the situation is more problematic, since the W–O–C angle (~144°) keeps the $\pi(\parallel)$ and $\pi(\perp)$ oxygen lone pairs nondegenerate. Given the short W–O bond in the fluoroalkoxide, O→W π-bonding is strong, so it becomes necessary to consider that one O→W bond involves the more potent $\pi(\perp)$ lone pair, while the second one uses the $\pi(\parallel)$ lone pair. Finally, it may be that the W–O–C planes are not orthogonal because this would aggravate repulsions between oxygen and chloride.

C



D_x D_y



III

The fact that the W–O–C angle in $W(OR_f)_2Cl_2L_2$ (145°) is considerably larger than that in $Cp^*Ru(PR_3)(OR_f)$ (124.6°)[3] is consistent with some use of the $\pi(\parallel)$ orbital; the open angle improves the overlap of $\pi(\parallel)$ with the d_π orbital. The presence of O→W π-bonding in $W(OR_f)_2Cl_2L_2$ is also supported by the fact that the W–O distance there (1.85 Å) is so much shorter than the essentially single W–O bonds in $[W(CO)_4(\mu_2\text{-}OR_f)]_2^{2-}$ (2.19 Å).[13]

Consequences for Reactivity. The lack of reaction of $W(OR_f)_2Cl_2L_2$ with water is surprising, as is the lack of NMR spectroscopic evidence for hydrogen bonding between this complex and water. Taken together, these observations indicate that the alkoxide ligands are not very Brønsted-basic. Since eq 1would lead to a

$$W(OR_f)_2Cl_2L_2 + H_2O \rightarrow WOCl_2L_2(L') + 2R_fOH \quad (1)$$

$$L' = R_fOH \text{ or } PMe_2Ph$$

very stable product, we suggest that the nonoccurrence of this reaction has its origin in a kinetic barrier: Since hydrolysis of alkoxides of electropositive metals is generally viewed as beginning by coordination of water, this suggests that $W(OR_f)_2Cl_2L_2$ is sufficiently saturated (~18 valence electrons) that precoordination of water is precluded.

A second conceivable mechanism is a direct attack of a water molecule on an alkoxide ligand. As our NMR study shows, there is not even hydrogen bonding between water and $W(OR_f)_2Cl_2L_2$, which would be the first required step for such a mechanism. Apparently, the strong O→W π-donation makes the oxygen inaccessible for electrophilic attack.

This resistance to adduct formation strongly contrasts with withdrawal of π-donation being a mechanism for facile Lewis base binding for later transition metal alkoxides.[3] We attribute such resistance by W(IV) to the electropositive and oxophilic character of this metal, which apparently makes a W–OR multiple bond stronger than the sum of W–OR and $W–OH_2$ single bonds. Steric crowding in a seven-coordinate water adduct must also be considered.

The *cis*-$W(OR_f)_2$ Case. The seemingly inscrutable feature of *all* $W(OR)_2Cl_2L_2$ compounds is the mutual *trans* positioning of two OR ligands. *Trans* stereochemistry would seem to require the two WOC planes in the OCH_2CF_3 compound to be orthogonal for optimum utilization of the two empty d_π orbitals. If the OR

---

[9] This same idea, of course, underlies the reaction of 17-valence-electron species by an associative mechanism. See: Trogler, W. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990; pp 306, 327. See also: Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6574.

[10] Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261.

[11] Rothfuss, H.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1993**, *212*, 165.

[12] These lone pairs will not be degenerate even when W–O–C = 180° due to their inequivalent interactions with the aryl π system.

[13] Darensbourg, D. J.; Mueller, B. L.; Reibenspies, J. H.; Bischoff, C. J. *Inorg. Chem.* **1990**, *29*, 1789.

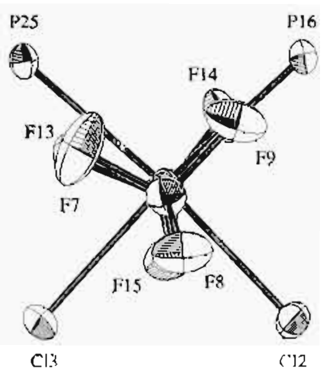
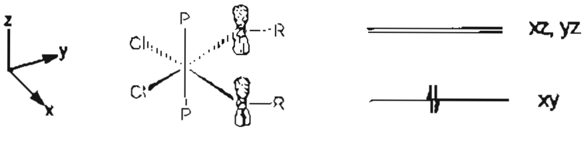


Figure 2. ORTEP drawing viewed down the O–W–O vector, showing the FCCOWOCCF chain lying in a plane which bisects the P–W–P angle.

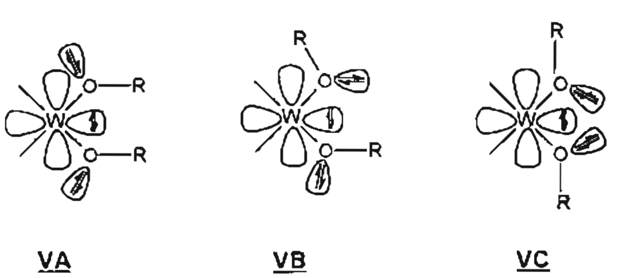
groups were *cis*, there would be no O→W π-donor competition and the two better oxygen lone pairs, π(⊥), would each find one empty d_π orbital.[14]

However, such a configuration would suffer significant repulsive interaction between the filled metal d orbital and the remaining lone pairs [π(∥)] of the oxygens. In the d_{xy}^2 case (**IV**), the d

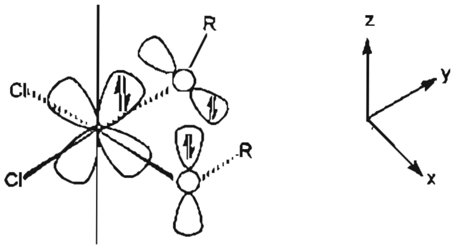


IV

electrons, both π(∥) and the R groups of the alkoxide ligands would be forced into the *xy* plane, creating strong filled–filled and steric repulsion (**V**). Alternatively, for d_{xz}^2 or d_{yz}^2 (depicted



in **VI** for d_{yz}^2), one "good" π-bond (along the *x* axis in **VI**) and one "bad" π-bond would be formed, the latter suffering the same filled–filled interaction as discussed for the d_{xy}^2 case.



VI

$W(OR_f)_2Cl_2(PMe_2Ph)_2$ and compounds **IA** and **IB** serve as a confirmation of the rule that in octahedral d^2 systems, two π donors seek a mutual *trans* arrangement, whereas only for a d^0 configuration is *cis* coordination preferred.[15]

Acknowledgment. This work was supported by the National Science Foundation. We thank James Mayer for stimulating discussions.

Supplementary Material Available: Listings of full crystallographic details and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

---

[14] This stereochemical feature of M(π donor)₂ molecules has been well studied. See: Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149 and references therein.

[15] Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29. Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203.