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Two Isomers of $WCl_3(PMe_2Ph)_3$ and Their Potential for Equilibration with $W_2Cl_6(PMe_2Ph)_n$

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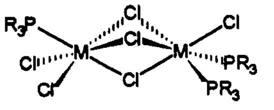
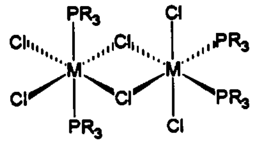
A new (comproportionation) synthesis of $WCl_3(PMe_2Ph)_3$, as well as the coexistence of two structural isomers, is reported. These are characterized by ^1H NMR spectroscopy and single-crystal X-ray diffraction. Equilibration of these two species is effected at 80 °C, with *mer* converting completely to *fac*. It is not possible to convert the WCl_3L_3 (L = PMe_2Ph) species to either of the known dimers $W_2Cl_6L_n$ (n = 3, 4). The *mer* → *fac* isomerization is shown to be catalyzed by WCl_4L_2 (but not by WCl_2L_4). The mechanism of the comproportionation synthesis of WCl_3L_3 strongly favors the *mer* isomer, and a mechanism is proposed to account for this. Photolysis of a mixture of $[WCl_3(PMe_2Ph)_2]_2$ in the presence of excess PMe_2Ph completely converts the dimer to *mer*-$WCl_3(PMe_2Ph)_3$. Mechanistic features which cause the stereoselectivity of this reaction are discussed. Cell parameters for *fac*-WCl_3L_3 (−165 °C): $a = 9.476(2)$ Å, $b = 18.091(5)$ Å, $c = 9.185(2)$ Å, $\alpha = 98.62(1)°$, $\beta = 101.53(1)°$, $\gamma = 93.49(1)°$ with $Z = 2$ in space group $P\bar{1}$. Cell parameters for *mer* WCl_3L_3 at −155 °C, $a = 16.031(3)$ Å, $b = 10.297(1)$ Å, $c = 17.913(3)$, $\beta = 113.86(1)°$, $Z = 4$, and space group $P2_1/c$.

Introduction

The synthesis of a solid sample of WCl_3L_3 (L = PMe_2Ph) by zinc reduction of WCl_4L_3 in THF has been reported, and X-ray diffraction revealed the isomer formed to have *mer* stereochemistry.[1] A subsequent publication[2] clarified the original spectral data by showing that the ^{31}P NMR signals of *mer*-WCl_3L_3 were broadened beyond detectability but that the ^1H NMR spectrum was diagnostic of the *mer* stereochemistry.[3] The original report was made at a time when it was known that both molybdenum and tungsten form a variety of phosphine derivatives of different stoichiometry ($[MCl_3(PR_3)_{1.5}]_2$ and $[MCl_3(PR_3)_{2.0}]_2$), which were known to have face-shared and edge-shared octahedral structures (I and II).[4–6] The earlier report[1] therefore mentions that efforts to convert *mer*-$WCl_3(PMe_2Ph)_3$ to dimers of the type I or II (130 °C in toluene) gave "... mixtures with a complex ^{31}P NMR spectrum which we were unable to analyze." This failure was puzzling given the reported synthesis of the compounds $W_2Cl_6(PMe_2Ph)_n$ with n = 3 and 4.[7] It remained of interest to attempt an equilibration of $WCl_3(PMe_2Ph)_3$ with these W_2 species. We report here a straightforward synthesis of *mer*-WCl_3L_3 by the comproportionation reaction of WCl_2L_4 with WCl_4L_2, along with its synthesis from the reaction between $W_2Cl_6L_4$ and excess phosphine. We also show that the *mer* isomer is the kinetic product and that this isomerizes to *fac*-WCl_3L_3 under rather specific conditions.



I



II

Experimental Section

All manipulations undertaken at ambient conditions (25 °C, 1 atm) were carried out in a glovebox under an argon atmosphere. The heating experiments were done in flame-sealed glass containers to avoid any contamination with oxygen. The glassware was vigorously flame dried and silylated. Solvents were dried over alkali metal and freshly distilled before use. Due to the high sensitivity of the described tungsten monomers to oxygen and water, any contamination results in the formation of corresponding amounts of $WOCl_2(PMe_2Ph)_3$.[8] ^1H NMR spectra were recorded on a Bruker AM 500 spectrometer at 500 MHz, $^{31}P\{^1H\}$ NMR measurements were performed on a Nicolet NT 360 spectrometer at 146.2 MHz using 85% H_3PO_4 as an external standard (0.0 ppm); negative phosphorus chemical shifts are upfield.

[●] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) Hills, A.; Hughes, D. L.; Leigh, G. J.; Prieto-Alcan, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1515.

(2) Yoon, K.; Parkin, G.; Hughes, D. L.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 769.

(3) The matter is significantly complicated by the ease with which H_2O (surface bound) converts the compound to $WOCl_2L_3$, whose sharp NMR lines are very evident, yet subject to misinterpretation. It has also been reported that water converts $WCl_4(PMe_2Ph)_3$ to $WOCl_2(PMe_2Ph)_3$. See: Carmona, E.; Sanchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797.

(4) (a) $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$: Cotton, F. A.; Fanwick, P. E.; Fitch, J. W. *Inorg. Chem.* **1978**, *17*, 3254. (b) $(LL)MoCl_2(\mu\text{-}SR)_2MoCl_2(LL)$: Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438. (c) $Mo_2Cl_6(dppe)_2$, $Mo_2Cl_6(dedppe)_2$, $W_2Cl_6(dppe)_2$: Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051. (d) $Mo_2Br_6(dppm)_2$, $Mo_2I_6(dppm)_2$, $Mo_2Cl_4I_2(dppm)_2$: Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J.; Price, A. C. *Inorg. Chem.* **1991**, *30*, 2509. (e) $Mo_2Cl_6(PEt_3)_4$: Mui, H. D.; Poli, R. *Inorg. Chem.* **1989**, *28*, 3609. (f) $Mo_2Cl_6(PMe_2Ph)_n$ (n = 3 and 4), $Mo_2Cl_6(PEt_3)_3$: Poli, R.; Mui, H. D. *Inorg. Chem.* **1991**, *30*, 65. (g) $Mo_2Cl_6(PMe_xEt_{3-x})_4$ (x = 0–3): Poli, R.; Gordon, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 6723. (h) $Mo_2X_6(dppe)_2$ (X = Cl, Br, I): Poli, R.; Owens, B. E. *Gazz. Chim. Ital.* **1991**, *121*, 413. (i) $Mo_2X_6(PMe_2Ph)_3$ (X = Br, I): Ahmed, K. J.; Gordon, J. C.; Mui, H. D.; Poli, R. *Polyhedron* **1991**, *10*, 1667.

(5) Mixed-metal dimers are also known. (a) $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$: Cotton, F. A.; James, C. A.; Luck, R. L. *Inorg. Chem.* **1991**, *30*, 4370. (b) $MoWCl_6(dppe)_2$, $MoWCl_6(\mu\text{-}dppm)_2$, $MoWCl_6(\mu\text{-}dmpm)_2$: Cotton, F. A.; Eglin, J. L.; James, C. A.; Luck, R. L. *Inorg. Chem.* **1992**, *31*, 5308.

(6) (a) $W_2Cl_6py_4$: Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760. (b) $Mo_2Cl_6(dmpm)_2$, $W_2Cl_6(dppm)_2$: Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046. (c) $W_2Cl_6(PEt_3)_n$ where n = 3 or 4: Chacon, S. T.; Chisholm, M. H.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1989**, *28*, 5. (d) $W_2Cl_6(PMe_3)_4$, $W_2Cl_6(PEt_3)_n$ where n = 3 and 4: Barry, J. T.; Chacon, S. T.; Chisholm, M. H.; DiStasi, V. F.; Huffman, J. C.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1993**, *32*, 2322.

(7) $W_2X_6(PR_3)_n$ (X = Cl or Br; PR_3 = PMe_3, PMe_2Ph, PBu_3; n = 4 or 3): Cotton, F. A.; Mandal, S. K. *Inorg. Chem.* **1992**, *31*, 1267.

(8) This "scavenging" of oxygen from any kind of oxygen source became most obvious in reactions carried out in flame-sealed NMR tubes at elevated temperatures. To avoid deforming the high-precision NMR tubes, these were not flame-dried but rather dried at 100 °C in an oven. Contamination with $WOCl_2L_3$, which was less than 1% at the beginning, increased by factors up to 10 for high temperatures (90–110 °C), implying that water surface-bound to the glass wall caused the formation of $WOCl_2L_3$.

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Table I. Crystallographic Data for *mer*-$WCl_3(PMe_2Ph)_3$ and *fac*-$WCl_3(PMe_2Ph)_3$

formula	$C_{24}H_{33}Cl_3P_3W$	$C_{24}H_{33}Cl_3P_3W$
space group	$P2_1/c$	$P\bar{1}$
a, Å	16.031(3)	9.476(2)
b, Å	10.297(1)	18.091(5)
c, Å	17.913(3)	9.185(2)
α, deg		98.62(1)
β, deg	113.86(0)	101.53(1)
γ, deg		93.49(1)
V, Å^3	2704.11	1518.78
Z	4	2
fw	704.65	750.73
T, °C	−155	−165
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.731	1.642
μ(MoK$_\alpha$), cm^{-1}	48.492	43.221
R^a	0.0292	0.0270
$R_w{}^b$	0.0312	0.0282

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o|^2]^{1/2}$ where $w = 4F^2/\sigma^2(F^2)$.

***fac*-, *mer*-$WCl_3(PMe_2Ph)_3$.** A 489-mg sample of $WCl_2(PMe_2Ph)_4$[9] (0.606 mmol) was dissolved in 25 mL of toluene and added to 365 mg of $WCl_4(PMe_2Ph)_2$[10] (0.606 mmol) in 50 mL of toluene. The orange solution was stirred for 12 h at 25 °C during which time the solution became pale brown. The solvent was removed under vacuum to yield a light brown powder. This solid is a mixture of *fac*- (~4%) and *mer*-$WCl_3(PMe_2Ph)_3$ (~96%) isomers contaminated by a trace of $WOCl_2(PMe_2Ph)_3$, which is responsible for the brown color. Washing three times with 3 mL of toluene removed the $WOCl_2(PMe_2Ph)_3$ impurity. The resulting yellow residue was *fac*- and *mer*-$WCl_3(PMe_2Ph)_3$ in ~50% yield. (Due to the high solubility of *mer*-$WCl_3(PMe_2Ph)_3$ in toluene, the washing procedure caused a considerable loss of this product.) To separate the two isomers, the residue was extracted twice with 3 mL of toluene. The remaining solid was completely dissolved in toluene. After 12 h at −20 °C, yellow crystals of *fac*-$WCl_3(PMe_3Ph)_3$ precipitated from the solution (yield: 3%). The combined extracts, which consisted mainly of *mer*-$WCl_3(PMe_2Ph)_3$ and only minor amounts of the *fac*-isomer, were concentrated and subsequently kept at −20 °C to give pure crystalline *mer*-$WCl_3(PMe_2Ph)_3$ after 12 h (yield: 30%). Abbreviations: lw - line width (Hz), br = broad, ax = axial, eq = equatorial, *o*, *m*, *p* = ortho, meta, and para. ^1H NMR (500 MHz, C_6D_6, 25 °C) for the *mer* isomer: δ −24.7 (br, lw = 57, 12H, CH_3), −16.4 (br, lw = 52, 6H, CH_3), 4.0 (t, J = 6 Hz, 1H, eq *p*), 6.2 (t, J = 5 Hz, 2H, ax *p*), 8.7 (br, lw = 50, 2H, eq *o*), 8.9 (d, lw = 8, 4H, ax *m*), 9.0 (d, J = 6, lw = 12, 2H, eq *m*), 12.2 (br, lw = 43, 4H, ax *o*). ^1H NMR (500 MHz, C_6D_6, 25 °C) for the *fac* isomer: δ −12.3 (br, lw = 26, 18H, CH_3); 3.0 (t, J = 7 Hz, lw = 2, 3H, *p*), 3.5 (mult, 6H, *m*), 10.4 (mult, 6H, *o*).

Due to incompleteness and misinterpretations in former publications, we report here the ^1H NMR data (500 MHz, C_6D_6, 25 °C) of WCl_4L_2,[11a,b] WCl_4L_3,[11a,b] WCl_2L_4,[11c] and $W_2Cl_6L_4$.[7] $WCl_4(PMe_2Ph)_2$: δ −27.6 (br, lw = 16, 12H, CH_3), 7.7 (t, J = 6 Hz, 2H, *p*), 8.2 (m, 4H, *m*), 10.4 (m, 4H, *o*). $WCl_4(PMe_2Ph)_3$: δ −12.6 (br, lw = 478, 18H, CH_3), 8.4 (br, lw = 14, 9H, *p* and *m*), 19.6 (br, lw = 24, 6H, *o*). $WCl_2(PMe_2Ph)_4$: δ 2.1 (br, lw = 298, 24H, CH_3), 7.6 (br, lw = 30, 8H, *m*), 8.5 (br, lw = 162, 8H, *o*), 10.8 (br, lw = 21, 4H, *p*). $W_2Cl_6(PMe_2Ph)_4$ ^1H NMR (500 MHz, toluene-d_8, 25 °C): δ 0.80 (s, lw = 6, 12H, CH_3), 1.25 (s, lw = 4, 12H, CH_3), 6.92–7.32 (m, 16H, phenyl), 8.04 (d, J = 7 Hz, 4H, phenyl). $^{31}P\{^1H\}$ NMR (146.2 MHz, toluene-d_8, 25 °C): δ −123.0 (s, br), −311.1 (s, br).

X-ray Structure Determinations. *mer*-$WCl_3(PMe_2Ph)_3$. A well-formed red crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −155 °C for characterization (Table I) and data collection (6° < 2θ < 45°). Standard inert atmosphere techniques were used during handling. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima corresponding to the monoclinic space group $P2_1/c$. Subsequent solution and refinement confirmed this choice. Data were collected using a continuous θ, two-θ scan with fixed background counts at each extreme of the scan. Equivalent data were averaged after Lorentz and polarization effects were applied. The structure was readily solved by direct methods (MULTAN78) and standard Fourier techniques. All hydrogen atoms were located in a difference Fourier on the non-hydrogen atoms and were included in the final least-squares refinement. A final difference Fourier was essentially featureless, the largest peaks being in the vicinity of the tungsten atom. The results are shown in Table II.

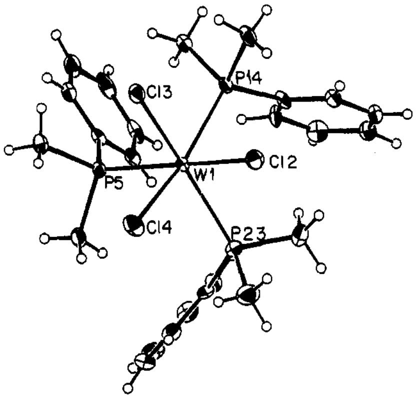

Figure 1. ORTEP drawing of *fac*-$WCl_3(PMe_2Ph)_3$, viewed down a pseudo-C_3 axis.

Table II. Selected Bond Distances (Å) and Angles (deg) for *mer*-$WCl_3(PMe_2Ph)_3$

W(1)–Cl(2)	2.4182(16)	W(1)–P(5)	2.5183(17)
W(1)–Cl(3)	2.4347(16)	W(1)–P(14)	2.5564(17)
W(1)–Cl(4)	2.3627(17)	W(1)–P(23)	2.5344(17)
Cl(2)–W(1)–Cl(3)	92.00(6)	Cl(3)–W(1)–P(23)	82.09(5)
Cl(2)–W(1)–Cl(4)	174.79(6)	Cl(4)–W(1)–P(5)	87.36(6)
Cl(2)–W(1)–P(5)	89.66(6)	Cl(4)–W(1)–P(14)	101.23(6)
Cl(2)–W(1)–P(14)	83.18(6)	Cl(4)–W(1)–P(23)	89.49(6)
Cl(2)–W(1)–P(23)	86.61(6)	P(5)–W(1)–P(14)	92.76(5)
Cl(3)–W(1)–Cl(4)	90.88(6)	P(5)–W(1)–P(23)	96.59(5)
Cl(3)–W(1)–P(5)	177.81(5)	P(14)–W(1)–P(23)	166.10(5)
Cl(3)–W(1)–P(14)	88.85(5)		

***fac*-$WCl_3(PMe_2Ph)_3 \cdot 0.5C_7H_8$.** A small yellow crystal was cleaved from a larger sample and affixed to the end of a glass fiber using silicone grease, and the mounted sample was then transferred to the goniostat where it was cooled to −165 °C for characterization (Table I) and data collection (6° < 2θ < 45°). Standard inert atmosphere handling techniques were used throughout the investigation. A systematic search of a limited hemisphere of reciprocal space located no symmetry or systematic absences indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the proper space group to be $P\bar{1}$. Data were collected using a standard moving crystal–moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged to yield 3629 observed data. The structure was solved by Patterson and Fourier techniques. A difference Fourier phased on the non-hydrogen atoms clearly located all hydrogen atoms, and these were included in the subsequent least-squares refinement. A final difference Fourier was essentially featureless, the largest peaks lying at the site of the tungsten atom. The results are shown in Table III and Figure 1.

Thermal Reaction of $W_2Cl_6(PMe_2Ph)_4$ with PMe_2Ph. $W_2Cl_6(PMe_2Ph)_4$[12] (0.020 g, 0.017 mmol) was dissolved in toluene-d_8 (0.5 mL) in an NMR tube. PMe_2Ph (16 μL, 0.113 mmol, >6 equiv) was added via syringe. The tube was frozen in liquid N_2, evacuated and flame-sealed. Subsequently, the sample was kept at 90 °C for 1 week. After this time, ^1H and $^{31}P\{^1H\}$ NMR spectra revealed the formation of WCl_4L_3 (2.6%), WCl_4L_2 (<0.3%), $WOCl_2L_3$ (26.0%), *fac*-WCl_3L_3 (1.7%), and *mer*-WCl_3L_3 (2.9%) in addition to the bulk amount of unreacted $W_2Cl_6L_4$ and free PMe_2Ph. The sample also showed a small amount of precipitate with the appearance of colloidal metal.

Photochemical Reaction of $W_2Cl_6(PMe_2Ph)_4$ + PMe_2Ph. A sample (Pyrex glass) identical to that above was irradiated for 4 h at 25 °C with

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(9) Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* **1990**, *28*, 326.

(10) The synthesis of $WCl_4(PMe_2Ph)_2$ was carried out in analogy to the preparation of $WCl_4(PMe_3)_3$.[9] The additional phosphine ligand in the resulting $WCl_4(PMe_2Ph)_3$ was removed at 110 °C under high vacuum for 1 h.[11b]

(11) (a) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1064. (b) Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 595. (c) Bell, B.; Chatt, J.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2492.

(12) The preparation of $W_2Cl_6(PMe_2Ph)_4$ followed the procedure for $W_2Cl_6(PEt_3)_4$.[6d]

Table III. Selected Bond Distances (Å) and Angles (deg) for *fac*-$WCl_3(PMe_2Ph)_3$

W(1)–Cl(2)	2.4416(16)	W(1)–P(5)	2.5172(16)
W(1)–Cl(3)	2.4475(16)	W(1)–P(14)	2.5101(16)
W(1)–Cl(4)	2.4545(15)	W(1)–P(23)	2.5109(17)
Cl(2)–W(1)–Cl(3)	89.84(5)	Cl(3)–W(1)–P(23)	163.76(5)
Cl(2)–W(1)–Cl(4)	91.75(5)	Cl(4)–W(1)–P(5)	80.94(5)
Cl(2)–W(1)–P(5)	170.86(5)	Cl(4)–W(1)–P(14)	163.63(5)
Cl(2)–W(1)–P(14)	82.70(5)	Cl(4)–W(1)–P(23)	83.30(6)
Cl(2)–W(1)–P(23)	78.30(5)	P(5)–W(1)–P(14)	102.83(5)
Cl(3)–W(1)–Cl(4)	86.05(6)	P(5)–W(1)–P(23)	106.06(5)
Cl(3)–W(1)–P(5)	84.22(5)	P(14)–W(1)–P(23)	110.41(5)
Cl(3)–W(1)–P(14)	78.57(5)		

a 450-W medium-pressure Hg lamp. After this time, ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete conversion of the dimer $W_2Cl_6L_4$ to a trace of $WOCl_2L_3$, 21.6% WCl_4L_3, 5.2% WCl_4L_2, and 73.2% *mer*-WCl_3L_3 (as estimated from ^1H NMR spectroscopy). Precipitation of a black solid suggests the possible formation of tungsten metal. In the ^1H NMR spectrum, no signals for *fac*-WCl_3L_3 were observed.

Results

Synthesis and Characterization of *fac*- and *mer*-$WCl_3(PMe_2Ph)_3$. We synthesized WCl_3L_3 by the comproportionation reaction of equimolar WCl_4L_2 with *trans*-WCl_2L_4.[13] This redox (atom transfer) reaction occurs within 12 h at 25 °C in toluene. The reaction produces two isomers, one pale yellow (*fac*) and the other *apparently* dark red (*mer*).[14] Each of these, when pure, was subsequently shown *not* to equilibrate (isomerize) detectably within 3 d at 25 °C. The comproportionation was quantitative and resulted in the formation of 96% *mer*- and 4% *fac*-WCl_3L_3 in addition to a trace of $WOCl_2L_3$.

A mixture of isomers can be separated since the *fac* isomer, with its larger dipole moment, is only poorly soluble in toluene, while the *mer* isomer is more soluble. Exhaustive washing of a mixture extracts mainly the *mer* isomer (and the ubiquitous impurity *mer*-$WOCl_2L_3$), leaving behind a solution highly enriched in the *fac* isomer. Crystallization gives pure *fac*-WCl_3L_3. Further concentration of this solution leads to a deposit of crystals of the *fac* and *mer* isomers.

NMR Spectra. Although no ^{31}P NMR signal is detectable for either isomer due to paramagnetism (d^3 configuration), the ^1H NMR spectra serve as a wholly satisfactory method for characterization of both structure, integrity in solution, and thermal reactivity. The range of chemical shifts of both compounds is +12 to −25 ppm, and line widths ($\Delta\nu_{1/2}$) range from 0.01 to 0.11 ppm. The *P*-methyl proton resonances are broader than the aryl signals,[15] and all resonances of the *fac* isomer are narrower than those of *mer*. The *fac* isomer shows one resonance for all methyls and one ortho, one meta and one para resonance, all consistent with C_3 symmetry. The *mer* isomer shows two methyl resonances (2:1 integrated intensity) and a total of six aryl resonances. For each isomer, the broadest aryl resonance(s) can be assigned to the *ortho* protons.

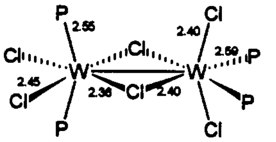
None of the resonances show resolvable coupling to phosphorus, but the meta and para protons generally show doublet and triplet structure (i.e., mutual coupling). The aryl hydrogen chemical shifts range from 2.99 to 12.2 ppm, and show no regular pattern from ortho to meta to para.

Temperature Dependance of the Chemical Shifts. The chemical shifts of methyl signals of the two isomers as well as of WCl_4L_2 are temperature-dependant. For the *mer* isomer, the signals at −24.7 and −16.4 ppm (25 °C) shift to −15.8 and −10.3 ppm at 90 °C. For the same temperatures, the *fac* isomer shows only a difference of 2.9 ppm from −12.3 to −9.6 ppm. The methyl signal of WCl_4L_2 at −27.6 ppm at 25 °C appears at −20.3 ppm at 90 °C.

Structures. The *fac* isomer is previously unknown, while the *mer* isomer was reported in 1991,[1] but its structure was soon thereafter[2] shown to suffer from compositional disorder: *mer*-$WOCl_2(PMe_2Ph)_3$ occupying some sites in the unit cell of $WCl_3(PMe_2Ph)_3$ and causing an erroneous shortening of (only one of) the W–Cl bond lengths in the *trans* Cl–W–Cl unit. Our redetermination of the structure of *mer*-$WCl_3(PMe_2Ph)_3$ shows these two W–Cl bond lengths (expected to be equivalent, based on chemical arguments and the average C_{2V} symmetry of this coordination geometry) are more similar than previously observed (2.418–2.363 *vs* 2.423–2.342 Å in ref 2), but nevertheless suffer some degree of the same effect.[16] There is excellent agreement between this work and that of Parkin on the remaining W–Cl distance and the three W–P distances.

The *fac* isomer displays C_3 symmetry of the bond lengths and angles of the inner coordination sphere.[17] Even the conformation of the phosphine substituents (Figure 1) is faithful to C_3 symmetry, with all phenyl groups in phase and projecting away from the WCl_3 end of the molecule and one methyl of an adjacent phosphine oriented over the face of each phenyl ring.

W–Cl and W–P distances with identical groups *trans* to themselves show insignificant differences in the *fac vs mer* isomers. For comparison, bond lengths in $[WCl_3(PMe_2Ph)_2]_2$ (C_2 crystallographic symmetry) are[7]



These show no major differences from the corresponding values in *fac*- and *mer*-$WCl_3(PMe_2Ph)_3$.

Conditions for *fac*/*mer* Isomerization. Isomerization of mixtures of *fac* and *mer* isomers or of pure *mer* (in the presence of WCl_4L_2 impurity) led to a complete conversion to *fac*-WCl_3L_3 at 80 °C. At temperatures above 90 °C, decomposition of the isomers to PMe_2Ph, WCl_4L_2, and WCl_4L_3 was detected (^1H NMR). Simultaneously, a black precipitate formed, which is presumably tungsten metal. We suggest that disproportionation (eq 1) may be the pathway for the observed decomposition. In

$$4WCl_3L_3 \rightarrow W\downarrow + 3WCl_4L_2 + 6L \qquad (1)$$

the presence of free PMe_2Ph, WCl_4L_2 is in equilibrium with WCl_4L_3.[11b] At no time or temperature was dimerization of WCl_3L_3 to $W_2Cl_6L_3$ (**I**) or $W_2Cl_6L_4$ (**II**) detectable by ^1H NMR.

Mechanism of the Comproportionation Reaction. To follow the course of the comproportionation of WCl_4L_2 and WCl_2L_4, the reaction was monitored by ^1H NMR. Spectra were taken after 10, 90, and 300 min and 24 h. Already after 10 min, a small amount of the *fac* isomer (4.4% of the formed WCl_3L_3)[18] was detected along with the major product *mer*-WCl_3L_3. Throughout the 24 h, the proportion of *fac*-WCl_3L_3 remained at 4% (±0.4) of the overall WCl_3L_3 formed. After 24 h, the consumption of

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(13) Rothfuss, H.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta*, in press.

(14) We find that the red color assigned to *mer*-$WCl_3(PMe_2Ph)_3$ is incorrect and is caused by varying amounts of purple $WOCl_2(PMe_2Ph)_3$ impurity. Both *fac*- and *mer*-$WCl_3(PMe_2Ph)_3$ are yellow.

(15) For other examples of ^1H NMR of phosphines on paramagnetic 4d and 5d metals, see: Over, D. E.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4643 and references cited therein.

(16) It is noteworthy that $10B_{iso}$ values in the *mer* isomer are 15, 16, and 19. While the Cl with the short W–Cl distance has the largest *B*, it is only marginally larger *and* all are smaller than the values (18–22) for the *fac* isomer. Finally, the thermal ellipsoid of Cl(4) of the *mer* isomer shows no elongation along the W–Cl bond, which reemphasizes[2] how difficult it can be to detect <20% oxo impurity in the present case.

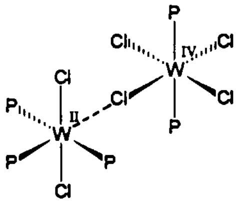
(17) The structure (and color) of the *fac* isomer shows no evidence for cocrystallization with *mer*-$WOCl_2L_3$ since the latter has the wrong molecular shape to incorporate in the growing lattice of *fac*-WCl_3L_3.

(18) All percentages reported here derive from integration of the single methyl signal of *fac*-WCl_3L_3 to the two methyl signals of the *mer* isomer in ^1H NMR.

the two starting materials was complete and only the two isomers were detected (and traces of $WOCl_2L_3$).

Due to its constant proportion over 24 h, we suggest that *fac*-WCl_3L_3 is formed during the comproportionation and is not a product of a subsequent isomerization. An isomerization *mer* → *fac* should show a dependence on the concentration of *mer*-WCl_3L_3 formed during the comproportionation. Thus, the proportion of *fac* would change over time. Furthermore, at 25 °C, solutions of pure *mer* isomer did not convert to *fac* over 24 h in the presence of WCl_4L_2, although this is an isomerization catalyst at higher temperatures (see below).

Given the fact that the very crowded *trans*-WCl_2L_4 dissociates phosphine to a small extent,[19] this reaction could go by a halide-bridged, inner-sphere mechanism. If so, the reaction proceeds through species **III**, and thus W^{II} immediately forms 1 mol of *mer* product. The fate of the former W^{IV} in **III** will then determine the degree of stereoselectivity in the reaction. If WCl_3L_2 (or **III** itself) were attacked by phosphine to give only *mer*-WCl_3L_3, then complete stereospecificity would result. Obviously, this attack is something less than perfect, and a small amount of *fac* is formed.



III

Mechanism of the Interconversion of the Isomers. A sample of *mer*-WCl_3L_3 (containing less than 5% *fac* isomer and 2% WCl_4L_2) was monitored over time in C_6D_6 by ^1H NMR. It is nearly unchanged over 4 h in the temperature range 40–70 °C in C_6D_6, but at 75 °C, it begins to show the growth of the *fac* isomer. After 12 h at 85 °C, it has been transformed mainly (>90%) to the *fac* isomer. This result shows that the *fac* isomer is thermodynamically favored.

To investigate the possible influence of tungsten complexes in different oxidation states on the interconversion of the two isomers,[20] three samples of *mer*-WCl_3L_3 in toluene-d_8 were flame-sealed in NMR tubes. All of them contained initially ~0.5% of the *fac* isomers as well as ~1.5% of WCl_4L_2.[21]

To one sample, WCl_4L_2 was added, to increase its proportion to 11% (sample W^{IV}). To the second sample was added WCl_2L_4, which consumed all WCl_4L_2 (by comproportionation) and kept the amount of WCl_2L_4 at 18% (sample W^{II}). The third sample was kept unchanged ("control"). Each sample was kept for 30 min in an oil bath at 50, 70, or 90 °C and was assayed by ^1H NMR spectra obtained with the probe at that temperature. Each was then heated for 30 min at 110 °C outside of the probe, and the ^1H NMR spectra were subsequently measured at 30 °C.

In all three cases, the ratio of *fac* to *mer* stayed almost unchanged up to 50 °C. For sample W^{II}, the amount of *fac*-WCl_3L_3 remained completely unchanged even at 90 °C. This observation shows that WCl_2L_4 is not an isomerization catalyst. It also makes clear that the interconversion of *mer* to *fac* is not thermally facile.

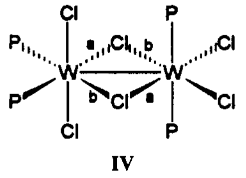
Comparison of the behavior of samples W^{IV} to the control shows that isomerization is catalyzed by WCl_4L_2. For both samples, the proportion of *fac*-WCl_3L_3 began to grow significantly at 70 °C, but in sample W^{IV}, containing more WCl_4L_2, the growth of *fac* is definitely faster than in the control. The amount of *fac*-WCl_3L_3 was 7.0% for W^{IV}, compared to 3.0% for the control. At 90 °C, the concentrations were 12.6% for W^{IV} and 5.3% for the control. After the heating period at 110 °C, sample W^{IV} contained 17.5% *fac*, whereas the control had only 7.7%.

In all three samples, partial decomposition of both isomers occurred at 110 °C (^1H NMR), with the formation of WCl_4L_3 and some WCl_4L_2 in sample W^{II}. As a consequence of the formation of WCl_4L_2 at 110 °C, sample W^{II} for the first time showed signals for *fac*-WCl_3L_3. Keeping the samples for 3 d at 130 °C caused complete decomposition of WCl_3L_3.

It is thus clear that pure WCl_3L_3 decomposes before it isomerizes or forms $W_2Cl_6L_4$ and free PMe_2Ph. Redox catalysis by WCl_4L_2 is required for isomerization.

Dimer-to-Monomer Conversion. The failure of WCl_3L_3 to form $W_2Cl_6L_4$ at higher temperatures (>90 °C) leads to the conclusion that either the kinetic barrier for the reaction lies too high (and decomposition of the W(III) monomers occurs first), or dimers **I** and **II** are not the thermodynamic product in this system. Therefore, we reinvestigated the possibility of cleaving the dimers[7] in the presence of free phosphine. Two identical samples of $W_2Cl_6L_4$ in d_8-toluene containing excess free phosphine (6.4P:1W_2) were flame-sealed into NMR tubes. One sample was heated for 1 week at 90 °C, at which point its composition was slightly changed (^1H and ^{31}P NMR assay). Small amounts of *mer*- (2.9%) and *fac*-WCl_3L_3 (1.7%) were detected by ^1H NMR. Again, the amount of produced $WOCl_2L_3$ increased by a factor >10 (as in the heating experiments with the monomers). Additionally, 2.5% of WCl_4L_3 and a trace of WCl_4L_2 (<0.3%), were observed; a black precipitate with a metallic appearance also formed. The thermal reaction of P with $W_2Cl_6L_4$ is thus characterized by a very high activation energy. Due to the fact that the reaction was carried out in a large excess of free PMe_2Ph, the equilibrium $WCl_4L_2 + P \rightleftharpoons WCl_4L_3$ was shifted far to the right, resulting in barely detectable amounts of WCl_4L_2. This is obviously the reason why there was still a higher yield of *mer*-WCl_3L_3 than of its *fac* isomer under these conditions. Apparently, WCl_4L_3 is not a catalyst for the interconversion of the two isomers, and the WCl_4L_2 present was insufficient to convert all *mer* to *fac*.

The second sample was irradiated (450-W medium-pressure Hg lamp, filtered through Pyrex glass) for 4 h at 25 °C. This showed bleaching (from the original purple-brown to pale yellow) and ^1H NMR evidence for the production of primarily *mer*-WCl_3L_3. Proton NMR signals for the *fac* isomer were absent, as were ^{31}P NMR signals for $W_2Cl_6L_4$. The amount of $WOCl_2L_3$ remained below 1% during the irradiation showing that only at temperatures >25 °C does a reaction with glass surface-bound water occur. Beside the cleavage of the dimer to *mer*-WCl_3L_3, the irradiation caused a concomitant disproportionation, leading to significant amounts of WCl_4L_3 (21.6%), WCl_4L_2 (5.2%), and a metallic-like precipitate. The fact that only the *mer* isomer (i.e., not the thermodynamic isomer) is produced indicates that this product is formed under conditions of kinetic control. An examination of the bridge bonds to be broken shows that scission either at **a** or at **b** will give only the *mer* isomer of WCl_3L_3. See structure **IV**. It is remarkable that such stereoselectivity is displayed, but a similar stereoselectivity was recently reported by



IV

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[19] Sharp, P. R. *Organometallics* **1984**, *3*, 1217. Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353.

[20] Isomerization of a kinetically-inert molecule is often greatly accelerated by one-electron transfer. See: Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037. Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1.

[21] Determination of the proportions of the tungsten monomers was done by ^1H NMR. For all but WCl_4L_3, integration of the methyl signal of the phosphine ligand was employed. Due to the very broad methyl resonance of WCl_4L_3, we used instead its ortho phenyl signal at 19.6 ppm, which is clearly distinct from all other phenyl signals.

Cotton and co-workers[22] in the cleavage of chloride-bridged Rh(III)–Rh(III) dimers.

Concluding Remarks

We have reported a stereoselective formation of *mer*-WCl_3L_3 by the comproportionation reaction involving WCl_4L_2 and WCl_2L_4. The redox reaction can be understood in terms of atom transfer by way of a mixed-valent chloride-bridged dimer, **III**. The isomerization of *mer*-WCl_3L_3 to *fac*-WCl_3L_3 is thermodynamically favored but does not occur readily upon thermolysis up to 90 °C in hydrocarbon solvents. However, above 50 °C, WCl_4L_2 acts as a catalyst for the isomerization of *mer*-to-*fac*-WCl_3L_3. Prolonged heating of WCl_3L_3 yields only products of decomposition but no formation of $W_2Cl_6L_4$ which could have been formed by (i) dissociation of PMe_2Ph and (ii) dimerization of two WCl_3L_2 fragments. However, photolysis of $W_2Cl_6L_4$ in the presence of excess PMe_2Ph did yield *mer*-WCl_3L_3. Thus, it is shown that the dinuclear compound can be converted to the mononuclear W(III) compound under appropriate conditions but we have found it impossible to form $W_2Cl_6L_4$ from WCl_3L_3.

Acknowledgment. This work was supported by the National Science Foundation.

Supplementary Material Available: Tables giving full crystallographic details, fractional coordinates and thermal parameters for *fac*- and *mer*-$WCl_3(PMe_2Ph)_3$ (7 pages). Ordering information is given on any current masthead page.

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[22] Cotton, F. A.; Eglin, J. L.; Kang, S.-J. *J. Am. Chem. Soc.* **1992**, *114*, 4015.