Origin of the Two Significantly Different W–Cl Bond Lengths for Chemically Equivalent Bonds in mer-[WCl₃(PMe₂Ph)₃]†

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The observation of two significantly different W–Cl bond lengths for chemically equivalent bonds, previously reported for mer-[WCl₃(PMe₂Ph)₃], has been reinterpreted as an artifact due to cocrystallization with an isostructural oxo impurity, cis-mer-[WOCl₂(PMe₂Ph)₃].

The synthesis and molecular structure of the tungsten(III) complex mer-[WCl₃(PMe₂Ph)₃] have been recently reported.[1] Tungsten(III) complexes are relatively rare and mer-[WCl₃(PMe₂Ph)₃] represents the first neutral mononuclear tungsten(III) derivative to be structurally characterized by X-ray diffraction (Fig. 1). Of particular interest, it was revealed that although the three W–P bond lengths [2.514(1), 2.536(1) and 2.555(1) Å] were similar, the three W–Cl bond lengths [2.295(2), 2.437(1) and 2.441(1) Å] were significantly different, with one being exceptionally short. The most surprising observation was that the short W–Cl bond length did not correspond to the unique chloro substituent that was located trans to PMe₂Ph, but rather corresponded to one of the chloro substituents that are mutually trans. Since this complex has a molecular plane of symmetry, the unexpected result that two chemically equivalent W–Cl bonds may have substantially different bond lengths [2.437(1) and 2.295(2) Å] is obtained. Here we report a reinvestigation of the molecular structure of mer-[WCl₃(PMe₂Ph)₃] and offer an explanation for the observation of significantly different W–Cl bond lengths for chemically equivalent bonds.

Results and Discussion

The subjects of the original reports of 'distortional'[2] or 'bond-stretch'[3] isomerism were molybdenum oxo complexes of the class cis-mer-[MoOCl₂(PR₃)₃]. We have recently reinvestigated the structures of these complexes in more detail, and determined that the observation of apparent 'isomers' with unusually long Mo=O bond lengths is an artifact due to cocrystallization with the trichloride impurity mer-[MoCl₃(PR₃)₃].[4] Incorporation of chloride into the oxo site results in an apparent increase of the 'Mo=O' bond length, since the chloride ligand is located at a much greater distance from the molybdenum centre (ca. 2.45 Å for Mo–Cl versus ca. 1.68 Å for Mo=O). In order to demonstrate further that cocrystallization may result in the determination of incorrect bond lengths, we have also investigated the apparent structural effects of doping a series of tris(3-tert-butylpyrazolyl)-hydroboratozinc complexes, [ZnX{HB(3Buᵗ-pz)₃}] (X = Cl, Br, I or CH₃) with isostructural impurities.[5] In each case, only a single 'atom' is observed at the disordered site, corresponding to an apparent Zn–X bond length that is a composite for the pair of complexes concerned.

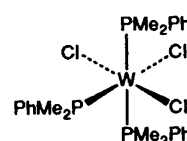In view of the above studies, and also the close similarity of mer-[WCl₃(PMe₂Ph)₃] to the aforementioned molybdenum

Fig. 1 Molecular structure of mer-[WCl₃(PMe₂Ph)₃]

system, we considered that a likely explanation for the observation of significantly different W–Cl bond lengths for chemically equivalent bonds may be cocrystallization of mer-[WCl₃(PMe₂Ph)₃] with the isostructural oxo complex cis-mer-[WOCl₂(PMe₂Ph)₃]. Thus, in an analogous fashion to the fact that the incorporation of chloride into the oxo site of cis-mer-[MoOCl₂(PMe₂Ph)₃] results in an apparent lengthening of the Mo=O bond,[4] the incorporation of oxo into one of the chloride sites of mer-[WCl₃(PMe₂Ph)₃] would be expected to result in an apparent shortening of the W–Cl bond.

Evidence that the above rationale may be likely was provided by examination of the ³¹P-{¹H} NMR spectrum. The spectrum of the oxo complex cis-mer-[WOCl₂(PMe₂Ph)₃][6] matched exactly, both in chemical shift and also W–P coupling constants, that reported for mer-[WCl₃(PMe₂Ph)₃].‡·[1] Since mer-[WCl₃(PMe₂Ph)₃] is paramagnetic, it is not unexpected that this species would not be readily observed by ³¹P-{¹H} NMR spectroscopy, thus resulting in only the diamagnetic cis-mer-[WOCl₂(PMe₂Ph)₃] impurity being detected. Although we could not observe ³¹P-{¹H} NMR resonances assignable to mer-[WCl₃(PMe₂Ph)₃], paramagnetically shifted ¹H NMR resonances are readily observed, in agreement with the original report. The most distinctive features of the ¹H NMR spectrum are the two resonances at δ −24.7 and −16.4 (in C₆D₆) in the ratio 2:1, assignable to the two sets of methyl groups of the trans- and cis-PMe₂Ph ligands, respectively. However, contamination by the diamagnetic oxo complex cis-mer-[WOCl₂(PMe₂Ph)₃] in this sample is revealed by the observation of two triplets at δ 1.92 and 1.67, and a doublet at δ 1.31, due to the methyl groups of the PMe₂Ph ligands.

The ¹H and ³¹P-{¹H} NMR studies described above clearly indicate that the bulk sample of mer-[WCl₃(PMe₂Ph)₃] is contaminated with cis-mer-[WOCl₂(PMe₂Ph)₃], the origin of which is unknown. As such, the possibility exists that cocrystallization may occur and thereby result in the observation of an apparently short W–Cl bond length.

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† Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx–xxv.

‡ However, it should be noted that the ¹J_{WP} coupling constants reported in ref. 1 are half the correct values.
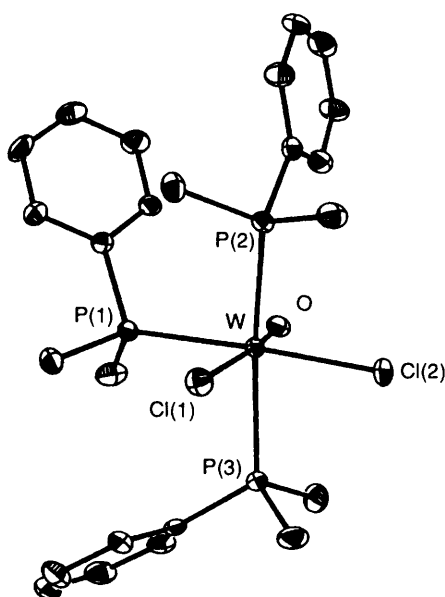
Fig. 2 An ORTEP drawing of cis-mer-[WOCl₂(PMe₂Ph)₃]

Fig. 3 An ORTEP drawing of mer-[WCl₃(PMe₂Ph)₃]

Table 1 Atom coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for cis-mer-[WOCl₂(PMe₂Ph)₃]

Atom	x	y	z	U*
W	2 131(1)	4 923(1)	1 708(1)	31(1)
P(1)	2 442(1)	6 603(2)	876(1)	37(1)
P(2)	3 535(1)	3 612(2)	1 909(1)	35(1)
P(3)	1 012(1)	6 229(2)	2 029(1)	37(1)
Cl(1)	3 290(1)	6 037(2)	2 924(1)	51(1)
Cl(2)	1 869(2)	3 374(2)	2 636(1)	55(1)
O	1 332(3)	4 303(5)	782(3)	44(2)
C(11)	1 428(6)	7 366(9)	120(5)	69(4)
C(12)	3 123(6)	7 972(8)	1 414(6)	63(5)
C(13)	2 975(5)	6 083(7)	206(4)	38(3)
C(14)	3 657(6)	6 769(9)	104(5)	62(4)
C(15)	4 032(7)	6 313(11)	-415(6)	74(5)
C(16)	3 737(7)	5 183(10)	-828(6)	74(5)
C(17)	3 048(6)	4 499(10)	-750(5)	65(4)
C(18)	2 683(6)	4 961(7)	-228(5)	45(3)
C(21)	4 530(5)	4 548(8)	2 001(5)	54(4)
C(22)	3 984(6)	2 718(8)	2 861(5)	58(4)
C(23)	3 433(5)	2 393(7)	1 147(4)	38(3)
C(24)	4 226(6)	1 883(8)	1 115(5)	55(4)
C(25)	4 158(7)	1 026(8)	517(6)	62(5)
C(26)	3 311(7)	673(9)	-77(6)	65(5)
C(27)	2 558(6)	1 137(8)	-37(6)	62(4)
C(28)	2 612(6)	1 984(8)	568(5)	56(4)
C(31)	1 245(7)	6 266(9)	3 104(5)	66(5)
C(32)	-134(6)	5 542(10)	1 525(6)	68(4)
C(33)	836(5)	7 928(7)	1 771(5)	40(3)
C(34)	93(5)	8 397(9)	1 123(5)	54(4)
C(35)	21(7)	9 679(10)	925(6)	71(5)
C(36)	697(7)	10 524(10)	1 385(7)	74(6)
C(37)	1 440(7)	10 088(8)	2 041(7)	75(5)
C(38)	1 519(6)	8 798(7)	2 232(5)	51(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The molecular structure of cis-mer-[WOCl₂(PMe₂Ph)₃] was determined by X-ray diffraction and found to be both isomorphous and isostructural with mer-[WCl₃(PMe₂Ph)₃]. An ORTEP drawing is presented in Fig. 2, and atomic coordinates are given in Table 1, with selected bond lengths and angles in Tables 2 and 3. The W=O bond length is 1.752(4) Å; however, in view of the problems associated with the corresponding molybdenum complexes,[4] we hesitate to attach
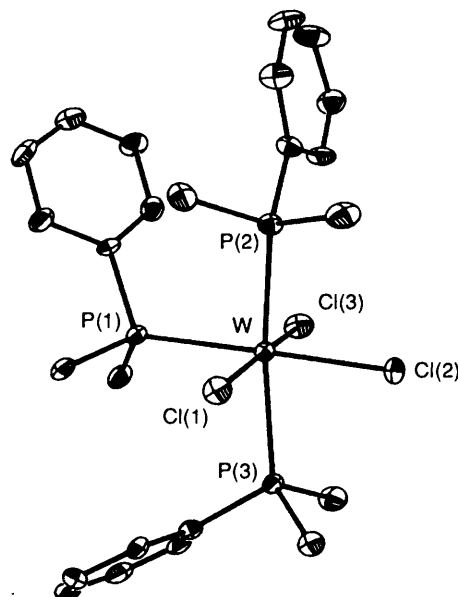
Table 2 Comparison of bond lengths (Å) for mer-[WCl₃(PMe₂Ph)₃] and cis-mer-[WOCl₂(PMe₂Ph)₃]

	[WCl₃(PMe₂Ph)₃]			
	a	b	c	[WOCl₂(PMePh)₃]^a
W-P(1)	2.513(5)	2.514(1)	2.513(5)	2.483(2)
W-P(2)	2.561(5)	2.555(1)	2.555(1)	2.538(2)
W-P(3)	2.542(5)	2.536(1)	2.536(1)	2.508(2)
W-Cl(1)	2.423(4)	2.437(1)	2.437(1)	2.493(2)
W-Cl(2)	2.428(5)	2.441(1)	2.442(1)	2.478(3)
W-Cl(3)	2.342(4)	2.295(2)	2.315(2)	
W-O				1.752(4)

^a This work. ^b Ref. 1. Labelling scheme is modified from the original report for comparison purposes. ^c Re-evaluated data from ref. 1 (see text).

Table 3 Selected bond angles ( ) for cis-mer-[WOCl₂(PMe₂Ph)₃]

P(1)-W-P(2)	94.2(1)	P(1)-W-P(3)	95.7(1)
P(2)-W-P(3)	160.5(1)	P(1)-W-Cl(1)	86.2(1)
P(2)-W-Cl(1)	80.0(1)	P(3)-W-Cl(1)	84.0(1)
P(1)-W-Cl(2)	175.2(1)	P(2)-W-Cl(2)	86.8(1)
P(3)-W-Cl(2)	81.9(1)	Cl(1)-W-Cl(2)	89.4(1)
P(1)-W-O	86.6(2)	P(2)-W-O	101.4(2)
P(3)-W-O	95.9(2)	Cl(1)-W-O	172.8(2)
Cl(2)-W-O	97.8(2)	W-P(1)-C(11)	114.4(4)

too much significance to this bond length, which is slightly longer than the average (1.70 Å) for monooxotungsten complexes.[7]

A crystal of mer-[WCl₃(PMe₂Ph)₃], shown by ¹H NMR spectroscopic analysis to come from a sample that was contaminated with ca. 20 molar $\%$ cis-mer-[WOCl₂(PMe₂Ph)₃], was investigated by X-ray diffraction. Atomic coordinates for mer-[WCl₃(PMe₂Ph)₃] are presented in Table 4, with selected bond lengths and angles in Tables 2 and 5. An ORTEP drawing is illustrated in Fig. 3. Although many of the bond lengths for the structure of mer-[WCl₃(PMe₂Ph)₃] reported here are similar to those in the previous report,[1] a significant difference is observed for the two trans W-Cl bonds, as illustrated in Table 2, which provides a comparison of the co-ordination environment for the two structures of mer-[WCl₃(PMe₂Ph)₃] and also for cis-mer-[WOCl₂(PMe₂Ph)₃]. Significantly, the very short W-Cl bond length [2.295(2) Å] reported for the original

**Table 4** Atom coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for mer-[WCl$_3$(PMe$_2$Ph)$_3$]

Atom	x	y	z	U*
W	2 199(1)	4 979(1)	1 825(1)	31(1)
P(1)	2 441(3)	6 612(4)	904(2)	34(2)
P(2)	3 548(3)	3 601(4)	1 915(2)	37(2)
P(3)	1 030(3)	6 272(4)	2 114(3)	36(2)
Cl(1)	3 321(3)	6 067(4)	2 978(2)	47(2)
Cl(2)	1 905(3)	3 413(4)	2 688(3)	51(2)
Cl(3)	1 050(3)	4 092(5)	683(3)	63(2)
C(11)	1 430(13)	7 359(17)	175(10)	58(9)
C(12)	3 113(14)	7 995(15)	1 401(22)	61(10)
C(13)	2 972(10)	6 036(15)	243(9)	37(7)
C(14)	2 641(12)	4 946(17)	−209(10)	51(7)
C(15)	2 997(15)	4 475(19)	−746(11)	62(9)
C(16)	3 684(15)	5 152(19)	−818(13)	73(11)
C(17)	4 004(15)	6 229(20)	−400(13)	80(12)
C(18)	3 662(13)	6 717(18)	149(12)	61(9)
C(21)	4 007(12)	2 673(18)	2 844(10)	64(9)
C(22)	4 539(11)	4 568(16)	2 041(12)	60(9)
C(23)	3 482(11)	2 429(14)	1 151(9)	40(7)
C(24)	4 242(14)	1 914(18)	1 111(11)	64(9)
C(25)	4 221(15)	1 062(21)	517(12)	70(10)
C(26)	3 399(18)	674(23)	−48(13)	81(12)
C(27)	2 614(14)	1 065(18)	20(12)	68(10)
C(28)	2 654(13)	1 933(15)	614(10)	53(8)
C(31)	−99(12)	5 559(18)	1 690(13)	66(10)
C(32)	1 282(13)	6 376(16)	3 182(9)	56(9)
C(33)	850(11)	7 967(15)	1 801(8)	37(7)
C(34)	92(12)	8 377(18)	1 176(11)	53(9)
C(35)	−3(15)	9 642(19)	929(13)	61(10)
C(36)	670(17)	10 511(19)	1 350(15)	63(12)
C(37)	1 412(16)	10 121(18)	1 968(14)	65(11)
C(38)	1 510(13)	8 857(16)	2 214(12)	52(9)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5 Selected bond angles (°) for mer-[WCl$_3$(PMe$_2$Ph)$_3$]

P(1)−W−P(2)	93.4(2)	P(1)−W−P(3)	96.4(2)
P(2)−W−P(3)	165.7(1)	P(1)−W−Cl(1)	89.7(1)
P(2)−W−Cl(1)	83.0(1)	P(3)−W−Cl(1)	86.7(1)
P(1)−W−Cl(2)	177.9(1)	P(2)−W−Cl(2)	88.4(2)
P(3)−W−Cl(2)	82.0(2)	Cl(1)−W−Cl(2)	91.7(1)
P(1)−W−Cl(3)	87.7(2)	P(2)−W−Cl(3)	101.2(2)
P(3)−W−Cl(3)	89.6(2)	Cl(1)−W−Cl(3)	175.2(2)
Cl(2)−W−Cl(3)	90.8(2)		
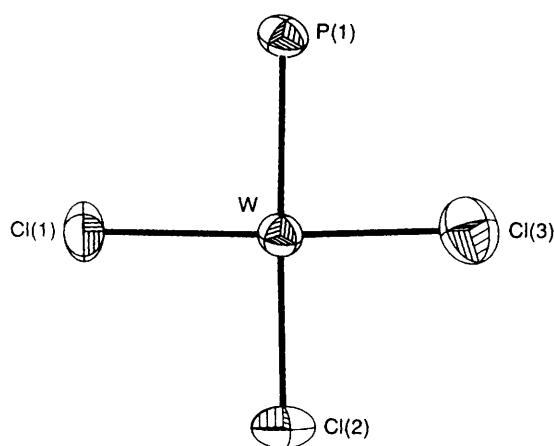
Fig. 4 Partial ORTEP drawing of mer-[WCl$_3$(PMe$_2$Ph)$_3$]

structure is not reproduced for the structure described here; instead, a substantially longer W–Cl bond length of 2.342(4) Å is observed. Although the two trans W–Cl bond lengths are still not identical, the difference between the two structures provides

good evidence that the apparently short W–Cl bond length is due to cocrystallization with cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$] impurity, the two structures differing slightly due to different levels of contamination. Indeed, the structure of pure mer-[WCl$_3$(PMe$_2$Ph)$_3$] remains to be determined.

The observation of two significantly different W–Cl bond lengths for chemically equivalent bonds in mer-[WCl$_3$(PMe$_2$-Ph)$_3$] is, therefore, an artifact due to cocrystallization with cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$]. The common belief that single crystals are invariably pure, coupled with the difficulty of detecting certain impurities by X-ray diffraction, accounts for the fact that this explanation was not originally considered.

The question arises as to why the presence of the oxo impurity in mer-[WCl$_3$(PMe$_2$Ph)$_3$] was not detected crystallographically, especially since it may be expected that disorder between oxygen and chlorine would be readily revealed by the presence of abnormal thermal parameters. Figs. 4 and 5 illustrate partial ORTEP drawings for mer-[WCl$_3$(PMe$_2$Ph)$_3$] and cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$] in a plane defined by the atoms shown. Clearly, the thermal parameters associated with Cl(3) of mer-[WCl$_3$(PMe$_2$Ph)$_3$] are larger than those for both Cl(1) and Cl(2). Larger thermal parameters would be expected for refining a site incorrectly as chlorine, if the site was partially occupied by an atom with lower atomic number, e.g. oxygen. However, are the thermal parameters of Cl(3) anomalously large? Alternatively, could the thermal parameters associated with Cl(1) and Cl(2) be anomalously small? It is not easy to answer this question definitively on the basis of the ORTEP drawing shown, although it may be assumed that Cl(1) and Cl(2) are correct since they are more similar.

Electron-density maps for mer-[WCl$_3$(PMe$_2$Ph)$_3$] and cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$] are shown in Figs. 6 and 7, respectively. The projections shown correspond to those of the partial ORTEP drawings in Figs. 4 and 5, and the contours are spaced at the same interval for both plots. It is apparent from Fig. 6 that there is slightly less electron density at Cl(3), with seven electron-density contours, compared with Cl(1) and Cl(2), each of which are characterized by nine contours. This observation is also supported by an electron-density difference map for mer-[WCl$_3$(PMe$_2$Ph)$_3$]. Reduced electron density at the site occupied by Cl(3) would naturally be expected if the site was partially occupied by an oxygen atom. However, it is not clear that this evidence alone would lead to a convincing suggestion that the site was compositionally disordered.

Supporting evidence for compositional disorder in mer-[WCl$_3$(PMe$_2$Ph)$_3$] has been obtained by refining the occupancies of a composite atom composed of both Cl and O located at the site 'Cl(3)'. This procedure resulted in the site occupancies Cl [0.80(3)] and O [0.20(3)], identical to the values estimated by ^{1}H NMR analysis of the bulk sample. It should be noted that performing a similar operation for the ordered site Cl(1) resulted in the occupancies Cl [1.01(1)] and O [0.01(1)], as expected for occupancy only by chlorine. Thus, for this system (although not necessarily for other systems), refining site occupancies provides a useful indication of compositional disorder.

We have also re-evaluated the data of Hills et al.[1] for which ^{1}H NMR spectroscopy also revealed the presence of the oxo impurity cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$]. Using a similar approach, the occupancy (S) of the Cl(3) atom site was allowed to vary, and an additional oxygen atom O(3) with partial occupancy ($1 - S$) was placed along the W–Cl(3) vector, with d(W–O) = 1.7 Å. After several cycles of refining the atom coordinates and either S or the thermal parameters of the Cl(3) and O(3) atoms, followed by two cycles on the whole structure, we found that the R factors were reduced significantly to $R = 0.041$ and $R' = 0.040$. Importantly, the site occupancy for Cl(3) refined to ca. 0.79, clearly supporting a model involving compositional disorder. The result of this refinement procedure was a slight increase in the apparent W–Cl(3) bond length to 2.315(2) Å, but the location of the oxygen atom was not precise.
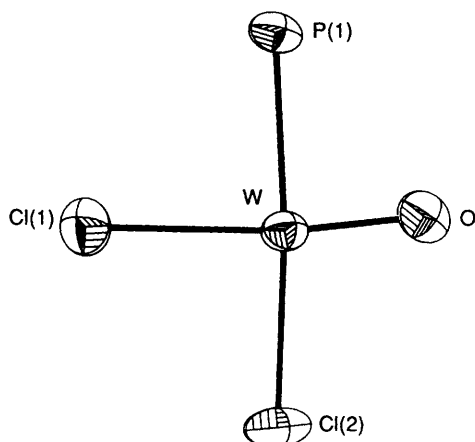
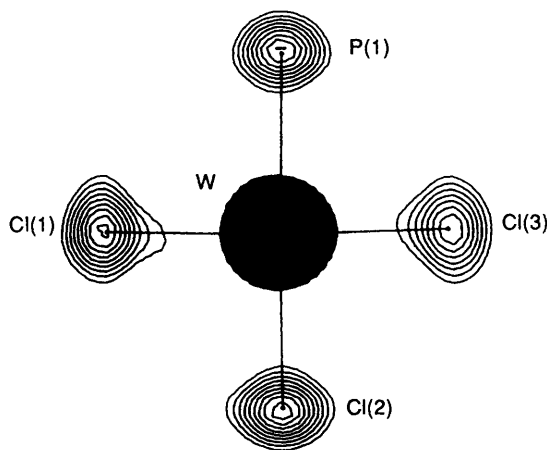**Fig. 5** Partial ORTEP drawing of cis-mer-[WOCl₂(PMe₂Ph)₃]

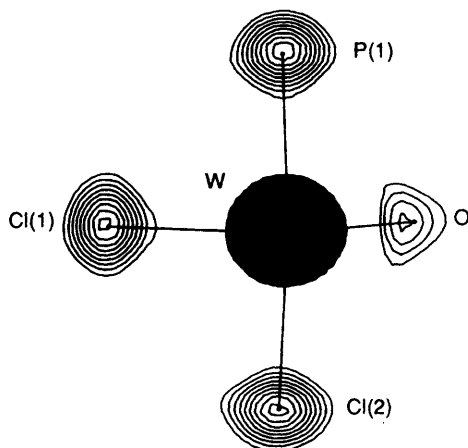**Fig. 6** Electron-density map for mer-[WCl₃(PMe₂Ph)₃] in the plane illustrated in Fig. 4

Fig. 7 Electron-density map for cis-mer-[WOCl₂(PMe₂Ph)₃] in the plane illustrated in Fig. 5

with d(W–O) = 1.61(2) Å. Changes in the rest of the molecule were not significant (see Table 2). This kind of analysis can only be taken so far, because in addition to the chlorine/oxygen replacement, the cocrystallized molecules are not of identical dimensions. Allowing only one set of structural parameters to vary during refinement is clearly an approximation, and it should be noted that the apparent W–Cl(3) bond length obtained by this procedure is still significantly different to that observed for W–Cl(1) [2.437(1) Å].

It is not entirely clear why this compositional disorder is confined to the Cl(3) position and is negligible at Cl(1). However, it is evident that the Cl(1) and Cl(3) sites are

inequivalent, due to the conformations of the substituents on the phosphine ligands, and it appears that the Cl(3) site is more sterically demanding than is the Cl(1) site. Therefore, on this basis, we suggest that Cl(3) would be the site that would be preferentially occupied by the smaller oxygen atom, and thereby allow disorder preferentially at only one site.

The effect that an impurity may have upon a structure determined by X-ray diffraction can be very subtle. We have shown that, depending upon the nature of the impurity, the most sensitive probe for the presence of an impurity at a compositionally disordered site may be the *apparent* bond length itself, and not the observation of abnormal thermal parameters.[4,5] Coupled with the common belief that single crystals are invariably pure, it is understandable how easy it is to misinterpret X-ray diffraction data for such cases. For example, the problem described above is reminiscent of that observed for the dimethyl derivative [Hf(η⁵-C₅H₅)₂Me₂] in which two significantly distinct Hf–Me bond lengths [2.318(8) and 2.382(7) Å] were originally reported.[8] This result has subsequently been reinterpreted as arising from cocrystallization with the *chloride* derivative [Hf(η⁵-C₅H₅)₂MeCl].[9]

Conclusion

The determination of two apparently different W–Cl bond lengths for the chemically equivalent bonds in mer-[WCl₃-(PMe₂Ph)₃] is an artifact. The origin of this artifact is cocrystallization with the oxo impurity cis-mer-[WOCl₂-(PMe₂Ph)₃]. Such contamination results in one of the chloro sites being partially occupied by an oxo ligand, thereby *apparently* shortening the W–Cl bond length.

Experimental

General Considerations.—All manipulations were performed using a combination of glove-box, high-vacuum or Schlenk techniques.[10] Solvents (except alcohols) were purified and degassed by standard procedures. The NMR spectra were measured on Varian VXR 300 and 400 spectrometers; ³¹P spectra are referenced relative to external H₃PO₄.

Preparation of cis-mer-[WOCl₂(PMe₂Ph)₃].—The complex cis-mer-[WOCl₂(PMe₂Ph)₃] was prepared by a modification of a previously reported synthesis.[11] A suspension of [WCl₄-(PMe₂Ph)₂] (2.0 g, 3.32 mmol) in tetrahydrofuran (thf) (100 cm³) was treated with PMe₂Ph (1.38 g, 10.5 mmol) giving a dark red solution. Water (0.06 cm³, 3.32 mmol) was added and the mixture stirred overnight at room temperature. A further equivalent of water (0.06 cm³, 3.32 mmol) was added and the mixture heated at 45 °C to complete the reaction. The mixture was filtered and the solvent was removed under reduced pressure. The sticky residue obtained was washed with pentane giving a purple solid. The latter was extracted into hot methanol and filtered. The filtrate deposited deep blue-purple crystals of pure cis-mer-[WOCl₂(PMe₂Ph)₃] upon cooling to room temperature (0.45 g, 20%). NMR data (C₆D₆): ¹H δ 1.49 [d, J_{PH} = 8.6, cis-P(CH₃)₂Ph], 1.85 [t, J_{PH} = 4.7, 2 trans-P[(CH₃)(CH₃)Ph], 2.11 [t, J_{PH} = 4.3, 2 trans-P(CH₃)(CH₃)Ph] and 7.0–7.6 [m, 3 PMe₂(C₆H₅)]; ³¹P-{¹H}, δ −23.5 (s, J_{PW} = 431, cis-PMe₂Ph) and −14.2 (s, J_{PW} = 340 Hz, 2 trans-PMe₂Ph).

Preparation of mer-[WCl₃(PMe₂Ph)₃].—This complex was prepared by a slight modification of the published method.[1] A solution of [WCl₄(PMePh)₃] (3.0 g, 4.1 mmol) in thf (25 cm³) was treated with zinc granules (0.53 g, 8.1 mmol) at room temperature. The mixture was stirred overnight at room temperature over which period the red solution became yellow-brown. The mixture was filtered and the solvent removed from the filtrate under reduced pressure giving a sticky brown residue. The residue was washed with pentane giving impure

Table 6 Crystal and intensity collection data

	cis-mer-[WOCl$_2$(PMe$_2$Ph)$_3$]	mer-[WCl$_3$(PMe$_2$Ph)$_3$]
Formula	C$_{24}$H$_{33}$Cl$_2$OP$_3$W	C$_{24}$H$_{33}$Cl$_3$P$_3$W
Formula weight	685.2	704.7
Lattice	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
$a/$Å	16.114(4)	16.228(3)
$b/$Å	10.413(2)	10.344(2)
$c/$Å	17.955(3)	18.100(3)
$\beta/^\circ$	114.50(1)	113.79(1)
$U/$Å^3	2741.4(9)	2780.0(7)
Z	4	4
$F(000)$	1352	1388
Crystal size/mm	0.36 × 0.60 × 0.72	0.12 × 0.48 × 0.60
2θ range/$^\circ$	3–45°	3–45°
$D_c/$g cm^{-3}	1.66	1.68
μ(Mo-Kα)/cm^{-1}	48.4	48.6
Octants collected	$h,k,\pm l$	$h,k,\pm l$
Number of independent reflections	3568	3635
Number of reflections with $F > 6\sigma(F)$	2759	2288
Number of parameters varied	281	281
R	0.0319	0.0597
R'	0.0421	0.0692

mer-[WCl$_3$(PMe$_2$Ph)$_3$] as a brown-green solid (1.5 g, 52%). Proton NMR analysis of this sample revealed that at this stage the product was already contaminated with cis-mer-[WOCl$_2$-(PMe$_2$Ph)$_3$]. Brown crystals were obtained by extraction into hot ethanol followed by cooling to room temperature. Proton NMR data (C$_6$D$_6$): δ −24.7 [br, 2 trans-P(CH$_3$)$_2$Ph], −16.4 [br, cis-P(CH$_3$)$_2$Ph] and 7.3–12.2 [several broad resonances, 3 PMe$_2$(C$_6$H$_5$)].

X-Ray Structure Determination Procedures.—Crystal data, data collection and refinement parameters for cis-mer-[WOCl$_2$-(PMe$_2$Ph)$_3$] and impure mer-[WCl$_3$(PMe$_2$Ph)$_3$] are summarized in Table 6. A typical procedure for the structure determination is as follows. A single crystal was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centred reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects. The structure was solved using Patterson and standard difference-map techniques on a Data General NOVA 4 computer using SHELXTL.[12] A weighting scheme of the form $w^{-1} = \sigma^2(F) + gF^2$ was employed for both structures. Space-group assignments were determined uniquely by systematic absences. Hydrogen atoms were included in calculated positions [d(C–H) = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)].

The composite 'atom' at the disordered site of impure mer-[WCl$_3$(PMe$_2$Ph)$_3$] was modelled by refining each atom of the composite pair with common positional and isotropic thermal parameters. The site occupancies were allowed to refine subject to the constraint that their sum was 1.0.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for both structures.

Acknowledgements

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