

## Structure of $\text{ReOFCl}_2(\text{PPh}_3)_2$ , a Crystallographic Pitfall

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### Introduction

Heavy-metal oxo-halo complexes containing bulky ligands like phosphines are prime candidates for hard-to-detect problems in crystal structure analysis. Molecular packing being largely controlled by the van der Waals envelope of the bulky ligand, the sites for the monoatomic groups can often be occupied in a disordered manner without introducing enough local strain to disrupt crystal architecture. This phenomenon has recently attracted considerable attention in connection with the debated question of bond-stretch isomerism. Parkin<sup>2</sup> has described various  $\text{MOCl}_2(\text{PR}_3)_3/\text{MCl}_3(\text{PR}_3)_3$  systems ( $M = \text{Mo}, \text{W}$ ) showing *compositional* disorder: two chemically different, but quasi-isostructural, molecules are randomly distributed over the crystallographic sites in the unit cell, the oxo group of one molecule being replaced with a Cl ligand of the other. *Compositional* disorder is an omnipresent threat with oxo-halo complexes of heavy transition metals, which commonly possess stable adjacent oxidation states. Another common problem encountered with oxo-halo complexes, even in pure phases, is *orientational* disorder. This is exemplified by the widely used  $\text{ReOCl}_3(\text{PPh}_3)_2$  compound:<sup>3</sup> depending on the solvent used for recrystallization, it can be isolated either as an ordered greenish-yellow monoclinic form or as a disordered yellow triclinic polymorph, in which one third of the molecules have the direction of their *trans* Cl–Re=O bonds interchanged (Chart 1).

Both types of disorder are usually not immediately identified, since the two fractional atoms on a given site do not give resolved peaks in electron density maps. Size, shape, or orientation of the thermal ellipsoids should in principle provide clues, but in most cases, they remain remarkably normal. In practice, the problem is detected by an abnormal metal–ligand bond length, which is the average of the M=O and M–X distances weighted by occupancy and atomic scattering power.

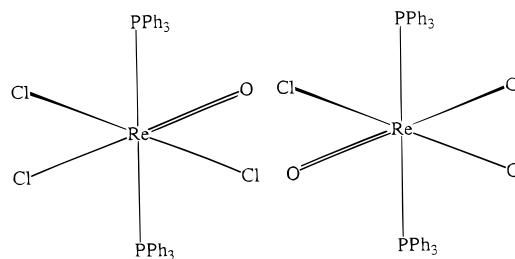
We wish to describe here the case of an apparently routine crystal structure, which turned out to show orientational disorder undetectable from any of the above clues, including interatomic distances.

### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR instrument as CsI pellets. Elemental analysis was performed at the Centre de Microanalyse du CNRS, Lyon, France. Magnetic measurements were obtained in the solid state at 25 °C by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet.

The compound was obtained when attempting to prepare  $\text{ReCl}_3(\text{MeCN})_3$  by adding 0.3 mL of 85%  $[\text{Et}_2\text{OH}]\text{BF}_4$  solution (Aldrich) to a mixture of  $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$  (0.252 g)<sup>4</sup> and acetonitrile (15 mL) in the glovebox. The vial was transferred to the Schlenk

### Chart 1



**Table 1.** Crystal Data and Structure Refinement for  $\text{ReOFCl}_2(\text{PPh}_3)_2$

formula	$\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{FOP}_2\text{Re}$	$\gamma$ , deg	111.068(5)
fw	816.65	$V$ , $\text{\AA}^3$	814.17(12)
space group	P1	$Z$	1
$T$ , K	293	$\rho_{\text{calc.}}$ , $\text{g cm}^{-3}$	1.666
$a$ , $\text{\AA}$	9.1945(6)	$\rho_{\text{obsd.}}$ , $\text{g cm}^{-3}$	1.62(2)
$b$ , $\text{\AA}$	10.0309(6)	$\mu$ , $\text{cm}^{-1}$	98.0
$c$ , $\text{\AA}$	10.2094(12)	$R1^a$	0.027
$\alpha$ , deg	109.585(8)	$wR2^a$	0.072
$\beta$ , deg	92.208(7)		

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

system and the solution was refluxed for 25 min. The clear orange-red solution was pumped to dryness under vacuum. The resulting solid was dissolved in  $\text{CH}_2\text{Cl}_2$ , and ether was added to precipitate green plates. The results below indicate that air leaked into the system at some point. Yield: 36%. Anal.: Calcd for  $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{FOP}_2\text{Re}$ : F, 2.33; Cl, 8.68; P, 7.59. Found: F, 2.28; Cl, 8.93; P, 7.46.

The same compound was prepared as an insoluble light-green powder forming immediately when 0.4 mL of 85%  $[\text{Et}_2\text{OH}]\text{BF}_4$  solution was added to a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{ReO}(\text{OEt})\text{Cl}_2(\text{PPh}_3)_2$  (0.199 g).<sup>5</sup> The solution was stirred for 15 min and then filtered.

The crystallographic work was carried out on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The crystal data are listed in Table 1. A whole sphere of data ( $2\theta \leq 140^\circ$ ) were collected, corrected for absorption (Gaussian integration),<sup>6</sup> averaged to the four-octant asymmetric unit (3079 reflections, 3028 with  $I > 2\sigma_I$ ), and corrected for the effects of Lorentz and polarization. The structure was solved by the direct methods of SHELXS-86<sup>7</sup> and  $\Delta F$  syntheses of SHELXL-93.<sup>8</sup> All non-hydrogen atoms were refined anisotropically. In the final interpretation, an averaged F/O scattering curve was used. Hydrogens were placed at idealized positions and recalculated after each cycle. The refined parameters are provided in the supporting information.

### Results and Discussion

The compound was first obtained as a byproduct of a reaction aimed at preparing  $\text{ReCl}_3(\text{MeCN})_3$  from  $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$ , by displacing the phosphine by protonation with  $[\text{Et}_2\text{OH}]\text{BF}_4$  in acetonitrile.<sup>9</sup> The raw material was recrystallized in a  $\text{CH}_2\text{Cl}_2$ /ether mixture and emerald green crystals, insoluble in all common solvents, appeared after a few days. From IR spectroscopy, it was clear that  $\text{PPh}_3$  was still present in the compound, which also showed a very strong band at  $995 \text{ cm}^{-1}$  probably due to a  $\nu(\text{Re}=\text{O})$  vibration. Thus, an oxo species had likely formed by air leaking into the system, but it could

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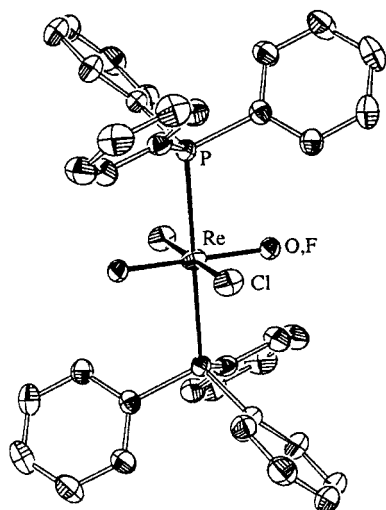
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**Figure 1.** ORTEP drawing of  $\text{ReOFCl}_2(\text{PPh}_3)_2$ . Ellipsoids are drawn at the 50% probability level. Hydrogens are omitted for simplicity. The O,F sites were originally believed to be fully occupied by oxygens of a  $\text{ReO}_2\text{Cl}_2(\text{PPh}_3)_2$  molecule. In the final interpretation, the F and O atoms are considered as statistically disordered over the two O, F positions related by the crystallographic inversion centre occupied by the Re atom. Distances (Å): Re–O,F 1.788(2), Re–Cl 2.3808(2), and Re–P 2.5213(8). Angles (deg): O,F–Re–Cl 89.91(8), O,F–Re–P 91.09(7), and Cl–Re–P 86.13(3).

not be  $\text{ReOCl}_3(\text{PPh}_3)_2$ , since the color of the crystals and the  $\nu(\text{Re}=\text{O})$  frequency did not correspond to either polymorph of this compound.<sup>3</sup>

Since NMR spectra could not be obtained for this insoluble material, an X-ray diffraction study was undertaken, and it first appeared to be a straightforward case. The structure solved easily in the centric space group  $P\bar{1}$  and refined normally down to  $R = 0.027$ . According to this model, the unit cell contained one molecule of what appeared to be *trans,trans,trans*- $\text{ReO}_2\text{Cl}_2(\text{PPh}_3)_2$ , with the Re atom sitting on a crystallographic inversion center (Figure 1). This molecule would then be a rare example of a dioxo–Re(VI) species, the only other case being the 4-dimethylaminopyridine (dmap) complex  $[\text{ReO}_2(\text{dmap})_4]^{2+}$  described by Brewer and co-workers.<sup>10</sup> Our Re–O distance (1.788(2) Å) was close that reported for the dmap compound (1.764(4) Å). This structure was consistent with the IR data. Besides the vibrations due to  $\text{PPh}_3$ , a  $\nu(\text{Re}–\text{Cl})$  band appeared at  $316\text{ cm}^{-1}$ .<sup>11</sup> The  $\nu(\text{Re}=\text{O})$  frequency ( $995\text{ cm}^{-1}$ ) seemed to be high, but not exceedingly so, considering that comparisons with related systems were not available.<sup>12</sup> A microanalysis of Cl (8.93%, calcd 8.68%) and P (7.46%, calcd 7.59%) supported our conclusions at this stage.

The first conflicting evidence came from magnetic susceptibility, showing the compound to be diamagnetic and thereby ruling out the Re(VI) oxidation state. Re-examination of the crystallographic results revealed no obvious anomaly: electron-density contours were normal, as were the thermal ellipsoids, and there were no suspect distances or angles. The possibility of a third polymorph of  $\text{ReOCl}_3(\text{PPh}_3)_2$  was ruled out, since statistical occupancy of the oxygen site by O and Cl would have led to a greater apparent bond length.<sup>2</sup> A possible alternative was that the crystal could actually contain a Re(V) *trans*- $\text{ReO}(\text{OH})\text{Cl}_2(\text{PPh}_3)_2$  molecule disordered over two orientations across the crystallographic inversion center. However, this

assumption disagreed with several other pieces of evidence: (i) no residual electron density was found near oxygen in the  $\Delta F$  map for a hydroxylic proton, (ii) there was no potential hydrogen-bond acceptor for the hypothetical Re–OH group, the shortest intermolecular contact with Cl or O in the unit cell being 3.577(2) Å; (iii) the OH group should produce a sharp  $\nu(\text{O}–\text{H})$  band above  $3000\text{ cm}^{-1}$  in the IR spectra, but this region was perfectly featureless, the only signals above  $2000\text{ cm}^{-1}$  being the very weak phosphine  $\nu(\text{C}–\text{H})$  absorptions at 3062 and  $3082\text{ cm}^{-1}$ .

The first useful clue was obtained when the IR data were scrutinized. In the  $500–600\text{ cm}^{-1}$  range, where  $\text{PPh}_3$  shows a set of bands,<sup>13</sup> it was noticed that the higher-frequency component was particularly strong and occurred at relatively high frequency ( $549\text{ cm}^{-1}$ ). This band could correspond to a  $\nu(\text{Re}–\text{OH})$  vibration,<sup>11</sup> but this possibility had been ruled out above. At this point, we found in the literature that  $\nu(\text{F}–\text{Re}–\text{F})$  bands appeared at 550 and  $510\text{ cm}^{-1}$  for  $[\text{ReCl}_2\text{F}_2(\text{NSSN})]^-$ .<sup>14</sup> Therefore, it became a definite possibility that some fluoro complexes could have been generated from  $[\text{Et}_2\text{OH}]\text{BF}_4$  and eventually oxidized to a mixed-halide  $\text{ReOFCl}_2(\text{PPh}_3)_2$  complex similar to the chloro–diiodo compound previously described.<sup>15</sup>

This assumption would be consistent with the crystallographic results, assuming that the O/F sites (Re–O(F) = 1.788(2) Å) are equally occupied by 9-electron F atoms (Re–F distance of 1.93 Å)<sup>14</sup> and 8-electron O atoms (Re=O distance of 1.66 Å).<sup>3</sup> The highest electron-density residual within 1 Å from the O/F atom ( $0.34\text{ e Å}^{-3}$ ) was much lower than the normal heavy-atom ripples ( $0.5–1.4\text{ e Å}^{-3}$ ) around Re and below the general background limit ( $0.57\text{ e Å}^{-3}$ ). Thus, the  $\Delta F$  map was insensitive to the disorder. An attempt to solve the structure in the noncentric group  $P1$  assuming an ordered  $\text{ReOFCl}_2(\text{PPh}_3)_2$  molecule failed, thereby confirming that the molecules are disordered in a centric  $P\bar{1}$  unit cell.

In order to positively identify this material, the compound was prepared by reacting  $\text{ReO}(\text{OEt})\text{Cl}_2(\text{PPh}_3)_2$ <sup>5</sup> with 1 equiv of  $[\text{Et}_2\text{OH}]\text{BF}_4$  in dichloromethane. The insoluble light green powder precipitated immediately and gave an IR spectrum identical to that obtained previously from the crystals. Fluorine microanalysis finally confirmed the composition proposed.

The geometry of the compound shows no unusual features. The Re–Cl and Re–P distances are similar to those reported for  $\text{ReOXCl}_2(\text{PPh}_3)_2$  compounds with  $X = \text{Cl}$  and  $\text{OEt}$ .<sup>3,16</sup>

In summary, this is a typical case of an apparently straightforward crystallographic study that could have led to wrong conclusions. Considering the large number of simple compounds similar to  $\text{ReOFCl}_2(\text{PPh}_3)_2$  described in the literature, problems of the type unraveled here are undoubtedly commonplace and have probably not been all identified yet.

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**Supporting Information Available:** Tables of complete crystal data, final coordinates, anisotropic temperature factors, and distances and angles for the crystallographic study (7 pages). Ordering information is given on any masthead page.

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