SUPPLEMENTARY INFORMATION FOR

Complexes of TaOCl₃ and TaSCl₃ with neutral N- and O-donor ligands - synthesis, properties and comparison with the niobium analogues.

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The disorder issue in the structure of [TaOCl₃(PPO₂)].

With two exceptions the molecule refines very nicely. The two exceptions are one of the terminal phenyl rings and the bridging ring. These both exhibit disorder which requires severe restraints and constraints to fit to a geometrically sensible result. This suggests that there may be an underlying crystallographic issue which we have been unable to identify.

Lower symmetry settings (all primitive and centred monoclinic options) and appropriate twin laws result in worse refinements. Another possibility is a modulated structure in which the disordered parts are modulated, however, examination of the diffraction pattern does not reveal the characteristic satellite reflections. The structure presented here has problematical parts of the structure modelled as disordered but care should be taken in any detailed interpretation of the refined model.

There are large residuals < 1 angstrom from the Ta metal which is probably a result of poorly modelled absorption (analytical), other residuals (positive and negative) are located in the vicinity of the modelled disorder. Full details of the refinement are in the Cif file.

[TaOCl₃(OPPh₃)₂]. There are some issues with this structure and the authors suspect that the true symmetry might be lower. However, at this time it has not been possible to resolve the potential issues and the structure is presented in the same space-group as the analogous Nb compound (CCDC code COJYEF) from the literature. The current space-group imposes disorder on one of the O/Cl sites and this has been modelled as split. The large difference peaks (both positive and negative) are indicative of the unresolved crystallographic issues and are left unexplained.

Crystal Data. C₃₆H₃₀Cl₃O₃P₂Ta, Mᵣ = 859.84, monoclinic, C₂/c (No. 15), a = 13.9027(2) Å, b = 12.95380(10) Å, c = 19.0339(2) Å, β = 95.0740(10)°, α = γ = 90°, V = 3414.44(7) Å³, T = 100(2) K, Z = 4, Z’ = 0.5, μ(MoKα) = 3.583, 68582 reflections measured, 4335 unique (Rint = 0.0247) which were used in all calculations. The final wR₂ was 0.2622 (all data) and R₁ was 0.1124 (I > 2(I)).
Supporting Spectroscopic Information

Figure S1 [TaOCl₃(1,10-phen)]  
Figure S2 [TaOCl₃(2,2’-bipy)]  
Figure S3 [TaOCl₃(OPPh₃)₂.0.5CH₂Cl₂]  
Figure S4 [TaOCl₃(dppmO₂)]  
Figure S5 [TaOCl₃(dppeO₂)]  
Figure S6 [TaOCl₃(PPO₂)]  
Figure S7 [TaSCl₃(1,10-phen)]  
Figure S8 [TaSCl₃(2,2’-bipy)]  
Figure S9 [TaSCl₃(OPPh₃)₂.0.5CH₂Cl₂]  
Figure S10 [TaSCl₃(dppmO₂)]  
Figure S11 [TaSCl₃(dppeO₂)]  
Figure S12 [TaSCl₃(PPO₂)]
Figure S1 [TaOCl₃(1,10-phen)]

Figure S1.1 [TaOCl₃(1,10-phen)] ¹H NMR spectrum (CD₂Cl₂, 298 K)

Figure S1.2 [TaOCl₃(1,10-phen)] IR Spectrum (Nujol)
Figure S2 $[\text{TaOCl}_3(2,2^{\prime}\text{-bipy})]$  

Figure S2.1 $[\text{TaOCl}_3(2,2^{\prime}\text{-bipy})]$ $^1$H NMR spectrum (CD$_2$Cl$_2$, 298 K) $^*$ = Protonated ligand (some overlap with product)

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Figure S2.2 $[\text{TaOCl}_3(2,2^{\prime}\text{-bipy})]$ IR Spectrum (Nujol)
Figure S3 \([\text{TaOCl}_3(\text{OPPh}_3)_2]\cdot2\text{CH}_2\text{Cl}_2\)

Figure S3.1 \([\text{TaOCl}_3(\text{OPPh}_3)_2]\cdot2\text{CH}_2\text{Cl}_2\) $^1$H NMR spectrum (CD$_2$Cl$_2$, 298 K)

Figure S3.2 \([\text{TaOCl}_3(\text{OPPh}_3)_2]\cdot2\text{CH}_2\text{Cl}_2\) $^{31}$P($^1$H) NMR spectrum (CD$_2$Cl$_2$, 298 K) L = ‘free’ ligand
Figure S3.3 $[\text{TaOCl}_3\{\text{OPPh}_3\}_2] \cdot 2\text{CH}_2\text{Cl}_2$ IR Spectrum (Nujol)

Figure S4 $[\text{TaOCl}_3\{\text{dppmO}_2\}]$

Figure S4.1 $[\text{TaOCl}_3\{\text{dppmO}_2\}]$ $^1\text{H}$ NMR spectrum (CD$_2$Cl$_2$, 298 K) Product sparingly soluble in CD$_2$Cl$_2$
Figure S4.2 \([\text{TaOCl}_3(dppmO}_2)]^{31}\text{P}\{^1\text{H}\}\) NMR spectrum (CD$_2$Cl$_2$, 298 K)

Figure S4.3 \([\text{TaOCl}_3(dppmO}_2)]\) IR Spectrum (Nujol)
Figure S5 $[\text{TaOCl}_3\text{(dppeO}_2\text{)}]$ 

Figure S5.1 $[\text{TaOCl}_3\text{(dppeO}_2\text{)}]$ $^1\text{H}$ NMR spectrum (CD$_2$Cl$_2$, 298 K)

Figure S5.2 $[\text{TaOCl}_3\text{(dppeO}_2\text{)}]$ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD$_2$Cl$_2$, 298 K)
Figure S5.3 $[TaOCl_3(dppeO_2)]$ IR Spectrum (Nujol)

Figure S6 $[TaOCl_3(PPO_2)]$

Figure S6.1 $[TaOCl_3(PPO_2)]$ $^{31}P\{^1H\}$ NMR spectrum (CD$_2$Cl$_2$, 298 K) * = Impurity likely caused by hydrolysis
Figure S6.2 \([\text{TaOCl}_3(\text{PPO}_2)]\) IR Spectrum (Nujol)

Figure S7. \([\text{TaSCl}_3(\text{1,10-phen})]\)

Figure S7.1 \([\text{TaSCl}_3(\text{1,10-phen})]\) \(^1\text{H}\) NMR spectrum (CD\(_2\text{Cl}_2\), 298 K) * = Protonated ligand
Figure S7.2 [{TaSCl3(1,10-phen)}] IR Spectrum (Nujol)

Figure S8 [{TaSCl3(2,2'-bipy)}]

Figure S8.1 [{TaSCl3(2,2'-bipy)}] $^1$H NMR spectrum (CD2Cl2, 298 K) * = Impurity likely caused by hydrolysis and protonated ligand
Figure S8.2 \([\text{TaSCl}_3(2,2’\text{-bipy})]\) IR Spectrum (Nujol)

Figure S9 \([\text{TaSCl}_3(\text{OPPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2\)

Figure S9.1 \([\text{TaSCl}_3(\text{OPPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2\) 1H NMR spectrum (CD_2Cl_2, 298 K)
Figure S9.2 \([\text{TaSCl}_3(\text{OPPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2\) \(^{31}\text{P}\)\(^{\text{H}}\) NMR spectrum (CD\(_2\)Cl\(_2\), 298 K); L = ‘free’ ligand.

Figure S9.3 \([\text{TaSCl}_3(\text{OPPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2\) IR Spectrum (Nujol)
Figure S10 $[TaSCl_3(dppmO_2)]$

Figure S10.1 $[TaSCl_3(dppmO_2)]$ $^1$H NMR spectrum (CD$_2$Cl$_2$, 298 K), Product sparingly soluble in CD$_2$Cl$_2$

Figure S10.2 $[TaSCl_3(dppmO_2)]$ $^{31}$P$[^1$H$]$ NMR spectrum (CD$_2$Cl$_2$, 298 K)
Figure S10.3 $[\text{TaSCl}_3(dppmO}_2)]$ IR Spectrum (Nujol)

Figure S11 $[\text{TaSCl}_3(dppeO}_2)]$

Figure S11.1 $[\text{TaSCl}_3(dppeO}_2)]$ $^1$H NMR spectrum (CD$_2$Cl$_2$, 298 K)
Figure S11.2 \([\text{TaCl}_3(\text{dppeO}_2)]\) $^{31}\text{P}^{[1}\text{H}]$ NMR spectrum (CD$_2$Cl$_2$, 298 K)

Figure S11.3 \([\text{TaCl}_3(\text{dppeO}_2)]\) IR Spectrum (Nujol)

Wavenumber (cm$^{-1}$)
Figure S12 \([\text{TaSCl}_3(\text{PPO}_2)]\)

Figure S12.1 \([\text{TaSCl}_3(\text{PPO}_2)]\) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD$_2$Cl$_2$, 298 K)

Figure S12.2 \([\text{TaSCl}_3(\text{PPO}_2)]\) IR Spectrum (Nujol)