SUPPLEMENTARY DATA FOR

Niobium tetrahalide complexes with neutral diphosphine ligands

Sophie L. Benjamin, Yao-Pang Chang, Andrew L. Hector, Marek Jura, William Levason, Gillian Reid and Gavin Stenning

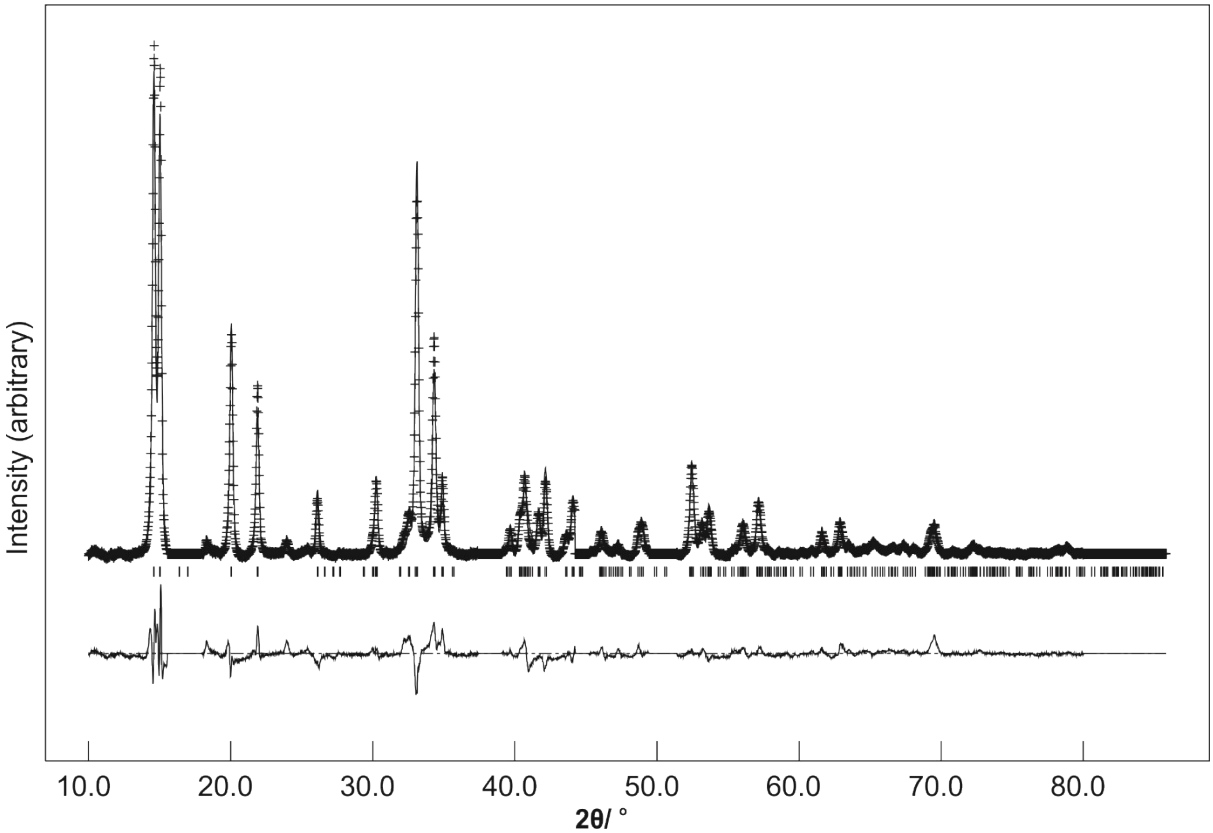

Figure S1. Fit to the PXRD data for $NbCl_4$ (R_{wp} = 6.92 %, R_p = 5.35%) fitted to the literature structure.[24] Crosses mark the data points, the upper continuous line the fit, the lower continuous line the difference and tick marks the positions of allowed reflections in *I*2/m with a = 8.1431(6) Å, b = 6.8405(4) Å, c = 8.8854(8) Å and β = 91.667(4)°. Literature values: a = 8.140(5), b = 6.823(4), c = 8.852(6) and β =91.92(5)°.

$[\{NbOCl_3\{Et_2P(CH_2)_2PEt_2\}\}_2(\mu\text{-}Et_2P(CH_2)_2PEt_2)]$

Crystals of this complex formed on attempted recrystallisation of $[Nb_2Cl_8(Et_2P(CH_2)_2PEt_2)_2]$ from diethyl ether. ^1H NMR (CD_2Cl_2, 295 K): δ = 1.1-1.37 (br, CH_3), 1.90-2.48 (br, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ = 21.2 [2P], 47.0 [4P]. IR (Nujol/cm^{-1}): 980 (Nb=O) 304, 293sh, 282sh (Nb-Cl).

Table S1 X-Ray crystallographic data.[a]

Compound	$[NbBr_4(Me_2PCH_2CH_2PMe_2)_2]$ $[NbOBr_4(NCMe)]$	$[\{NbOCl_3\{Et_2P(CH_2)_2PEt_2\}\}_2$ $\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$
Formula	$C_{14}H_{35}Br_8NNb_2OP_4$	$C_{30}H_{72}Cl_6Nb_2O_2P_6$
Formula weight	1182.41	1049.21
Crystal system	Tetragonal	Monoclinic
Space group	P4/n	$P2_1/c$
a/ Å	12.011(3)	9.8162(3)
b/ Å	12.011(3)	11.6449(3)
c/ Å	11.065(4)	20.2185(14)
α/deg	90	90
β/ deg	90	95.496(7)
γ/ deg	90	90
U/ $Å^3$	1596(1)	2300.5(1)
Z	2	2
μ(Mo-$K_α$)/mm^{-1}	10.942	1.082
F(000)	1112	1084
Total no. reflections	10587	20644
Unique reflections	1835	5247
R_{int}	0.0372	0.0349
No. of parameters, restraints	74, 0	214, 1
R_1[b] [Io>2σ(Io)]	0.0188	0.0288
R_1 (all data)	0.0198	0.0358
wR_2[b] [Io >2σ(Io)]	0.0486	0.0637
wR_2 (all data)	0.0490	0.0665

[a] Common items: temperature = 100 K; wavelength (Mo-$K_α$) = 0.71073 Å; θ(max)= 27.5°.

[b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|F\sigma|$; $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$

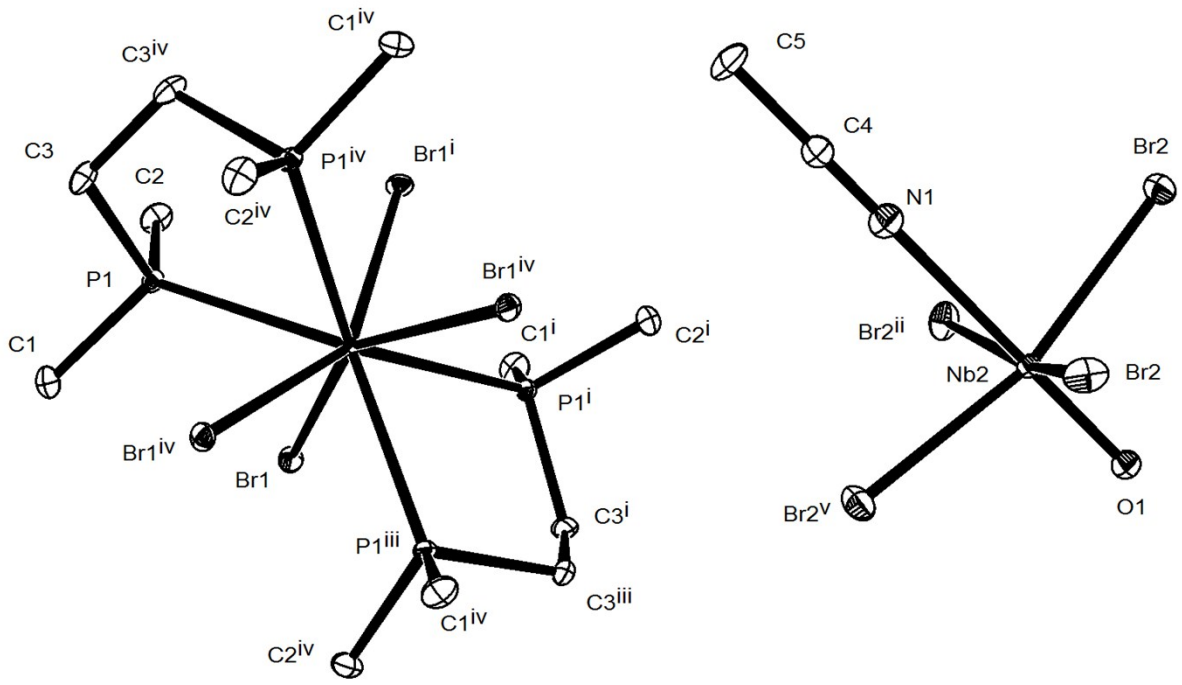

Figure S2 The structure of $[NbBr_4(Me_2PCH_2CH_2PMe_2)_2][NbOBr_4(MeCN)]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cation: Nb1–Br1 = 2.6017(6), Nb1–P1 = 2.7079(9), Br1–Nb1–$Br1^{iv}$ = 94.656(4), P1–Nb1–$P1^{iv}$ = 71.78(3). Anion: Nb2–O1 = 1.699(3), Nb2–N1 = 2.441(4), Nb2–Br2 = 2.5535(7), Br2–Nb2–Br2 = 88.968(3), O1–Nb2–Br2 = 97.712(11), O1–Nb2–N1 = 180.0. Symmetry operation i = ½+y, 1-x, 1-z; ii = ½-y, x, z; iii = 1.5-x, ½-y, z; iv = 1-y, -½+x, 1-z; v = y, ½-x, z; v = ½-y, x, z.

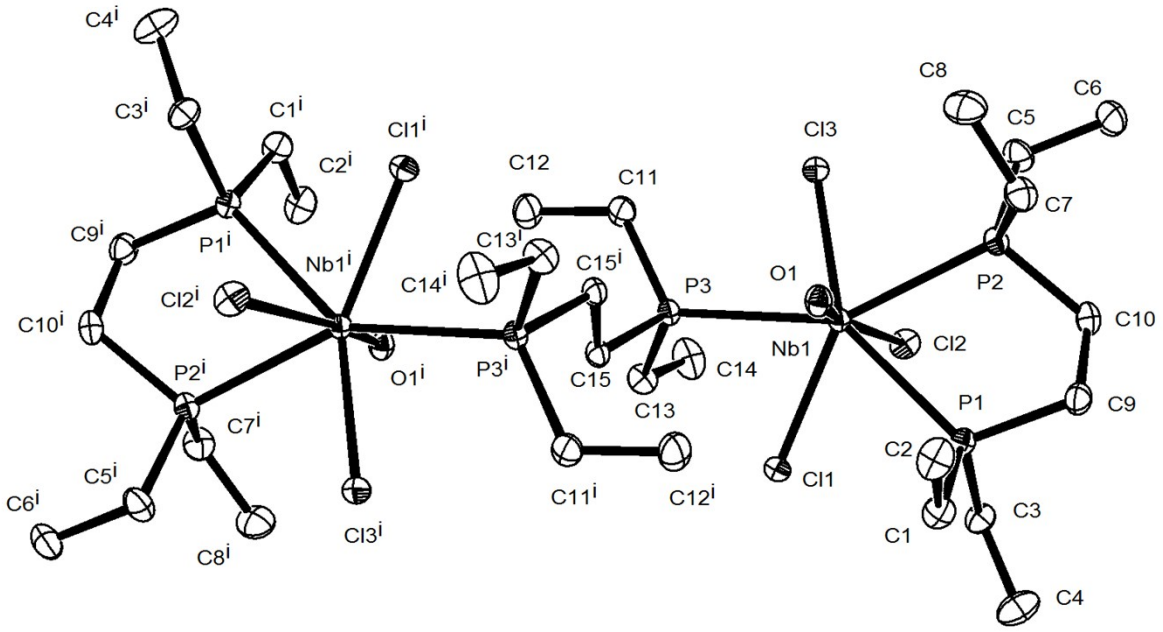

Figure S3 The structure of the centrosymmetric [{$NbOCl_3${$Et_2P(CH_2)_2PEt_2$}}$_2$(μ-$Et_2P(CH_2)_2PEt_2$)] showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.723(1), Nb1–Cl3 = 2.4717(6), Nb1–Cl1 = 2.4956(6), Nb1–Cl2 = 2.5774(6), Nb1–P2 = 2.6703(6), Nb1–P1 = 2.7007(6), Nb1–P3 = 2.7627(6), O1–Nb1–Cl3 = 94.84(6), O1–Nb1–Cl1 = 96.44(6), Cl3–Nb1–Cl2 = 87.64(2), Cl1–Nb1–Cl2 = 89.49(2), O1–Nb1–P2 = 88.83(5), Cl3–Nb1–P2 = 74.62(1), O1–Nb1–P1 = 88.57(5), Cl1–Nb1–P1 = 69.05(1), Cl2–Nb1–P1 = 81.51(1), P2–Nb1–P1 = 70.57(1), O1–Nb1–P3 = 94.05(5), Cl3–Nb1–P3 = 75.31(2), Cl1–Nb1–P3 = 70.34(2), Cl2–Nb1–P3 = 100.09 (2). Symmetry Operator i = -x, -y, -z.