ESI

Soft diphosphine and diarsine complexes of niobium(V) and tantalum(V) fluorides: synthesis, properties and comparisons with the corresponding chlorides.

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$[NbCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2][NbCl_5(OEt)]$. Orange-red crystals of $[NbCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2][NbCl_5(OEt)]$ were grown from a CH_2Cl_2 solution of $[NbCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ $[NbCl_6]$ by vapour diffusion of diethyl ether. The ethoxide group either comes from EtOH impurity in the diethyl ether or by C-O bond cleavage in the ether. The complex is isomorphous with $[TaCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ $[TaCl_5(OEt)]$.[S1]

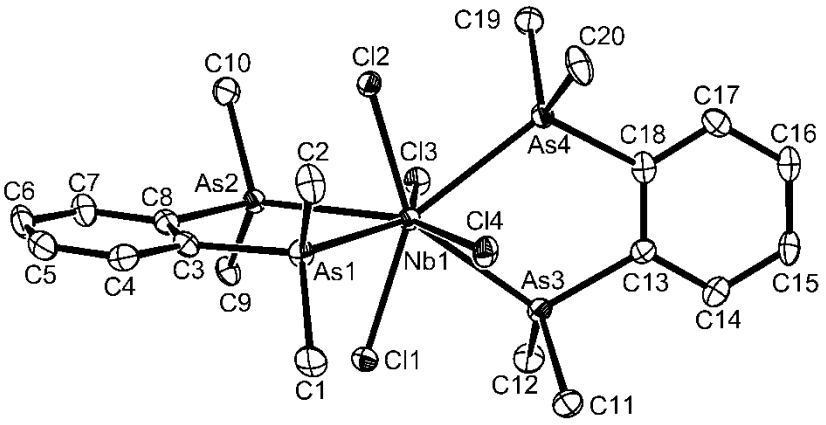

Fig. S1 The cation in $[NbCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2][NbCl_5(OEt)]$. ORTEP drawn with 50% probability level ellipsoids. Selected bond lengths (Å) and angles (°): Nb1─Cl2 = 2.4215(16), Nb1─Cl4 = 2.4277(14), Nb1─Cl1 = 2.4370(15), Nb1─Cl3 = 2.4399(15), Nb1─As2 = 2.7302(13), Nb1─As3 = 2.7351(14), Nb1─As1 = 2.7491(10), Nb1─As4 = 2.7501(11), As2─Nb1─As1 = 73.03(3), As3─Nb1─As4 = 72.66(3), Cl2─Nb1─Cl4 = 94.04(5), Cl4─Nb1─Cl1 = 95.47(5), Cl2─Nb1─Cl3 = 95.54(5), Cl1─Nb1─Cl3 = 94.37(5).

$[NbCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2][NbOCl_4(MeCN)]$: crystals were obtained as described in the main text. The cation geometry is essentially identical to that described for $[NbCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]Cl$ and the anion is a distorted octahedron.

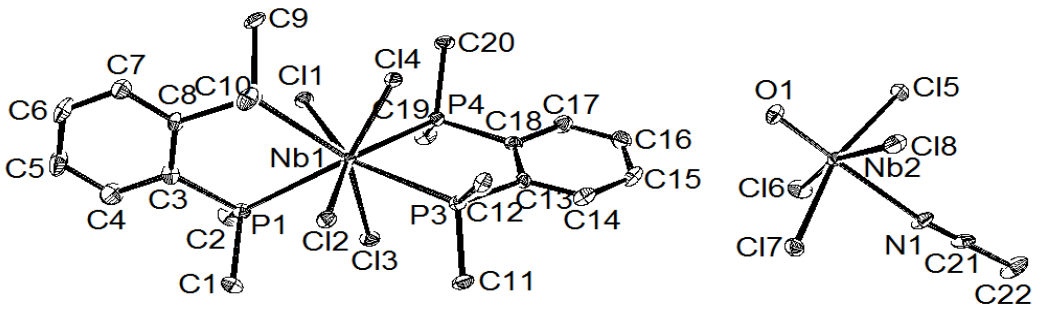

Fig. S2. The ions of $[NbCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2][NbOCl_4(MeCN)]$, ellipsoids are drawn at the 40% Level. Selected bond lengths (Å) and angles (°) Cation: Nb1─Cl2 = 2.4378(17), Nb1─Cl4 = 2.4385(17), Nb1─Cl3 = 2.4392(17), Nb1─Cl1 = 2.4444(17), Nb1─P4 = 2.6772(18), Nb1─P1 = 2.6824(19), Nb1─P2 = 2.6884(18), Nb1─P3 2.6904(18), Cl2─Nb1─Cl4 = 92.67(6), Cl2─Nb1─Cl3 = 95.36(6), Cl4─Nb1─Cl1 = 96.76(6), Cl3─Nb1─Cl1 = 95.11(6), P1─Nb1─P2 = 72.57(5), P4─Nb1─P3 = 72.76(5),

Anion: Nb2─O1 = 1.700(4), Nb2─Cl8 = 2.3836(17), Nb2─Cl6 = 2.3893(17), Nb2─Cl5 = 2.4090(18), Nb2─Cl7 = 2.4113(18), Nb2─N1 = 2.474(6), O1─Nb2─Cl8 = 98.05(15), O1─Nb2─Cl6 = 97.35(15), O1─Nb2─Cl5 97.81(16), Cl8─Nb2─Cl5 = 88.55(7), Cl6─Nb2─Cl5 = 88.73(7), O1─Nb2─Cl7 = 99.90(16), Cl8─Nb2─Cl7 = 88.64(6), Cl6─Nb2─Cl7 = 89.35(6).

Table S1 X-Ray crystallographic data.

Compound	$[NbCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$ $[NbCl_5(OEt)]$	$[NbCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]$ $[NbOCl_4(CH_3CN)]\cdot 0.5CH_2Cl_2$
Formula	$C_{22}H_{37}As_4Cl_9Nb_2O$	$C_{22.5}H_{36}Cl_9NNb_2OP_4$
M	1122.07	965.27
Crystal system	triclinic	orthorhombic
Space group (no.)	P-1 (no. 2)	Pbcn (no. 60)
a /Å	12.144(4)	15.733(2)
b /Å	12.649(4)	14.914(2)
c /Å	14.145(5)	32.080(5)
α/ °	108.902(15)	90
β /°	108.00(3)	90

γ/°	102.027(5)	90
U /Å^3	1836.4(11)	7527.2(18)
Z	2	8
μ(Mo-K$_\alpha$ /mm^{-1}	4.874	1.439
F(000)	1088	3848
Total number reflns	17441	29471
R_{int}	0.0418	0.0871
Unique reflns	8354	7372
No. of params, restraints	343, 0	366, 0
R_1, wR_2 [$I > 2\sigma(I)$]	0.0507, 0.0745	0.0745, 0.1024
R_1, wR_2 (all data)	0.0623, 0.0791	0.1042, 0.1111

References.

S1. J. C. Dewan, D. L. Kepert, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.,* 1975, 2031.