The synthesis of a novel heterobimetallic amidotungsten–antimony complex

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ABSTRACT

Reaction of $Li_2[W(NBu^t)_4]$ with two equivalents of $SbCl_3$ at $-78\ °C$ yields orange-red crystals of the novel heterobimetallic $Sb_2W(NBu^t)(\mu_2-NBu^t)(\mu_3-NBu^t)_2Cl_3(\mu_2-Cl)$ (**1**) in low yield (25%). From a 1:4 reaction stoichiometry, in addition to **1** crystals of $[W(NBu_2^t)(H_2NBu^t)Cl_2]_2$. $trans$-$[Sb(Cl)(\mu-NBu^t)]_2$ (**2**), $[W(NBu_2^t)(H_2NBu^t)Cl_2]_2.SbCl_3$ (**4**), $Sb_2W_3Cl_7(\mu_2-O)(\mu_3-O)_2(NBu_2^t)_3(NHBu^t)(\mu_2-NBu^t)_2$ (**3**) and $Sb_2W(NBu^t)$-$(\mu_2-NBu^t)(\mu_3-NBu^t)_2Cl_3(\mu_2-Cl)$. $Sb_2W_3Cl_7(\mu_2-O)(\mu_3-O)_2(NBu^t)_3(NHBu^t)(\mu_2-NBu^t)_2$ (**5**) have been characterised.

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1. Introduction

Tungsten imido(amido) complexes $W(NR)_2(HNR)_2$, with an all-nitrogen coordination sphere about the metal and two strong W=N bonds, are emerging as an important class of compound for the preparation of tungsten nitride [1]. It is somewhat surprising, therefore, that the chemistry of related heterobimetallic systems has remained largely dormant since the early work of Wilkinson and co-workers [2] and Nugent [3,4], since these in turn may act as precursors to ternary nitride materials. Indeed, since the early structural characterisation of $Li_2[W(NBu^t)_4]$, $[W_2Cu(N-Bu^t)_2(\mu-NBu^t)_6(NHBu^t)_2][BF_4]$ and $W[(\mu-NBu^t)_2(MX_2)]_2$ (X = Cl, Me; M = Al, Ga) [2], in the 1980s, only $Sn[W(\mu-NBu^t)_2(NBu^t)_2]$ [5] has been added until our recent reports on $W(NBu^t)_4[Rh(COD)]_2$, $W(NBu^t)_4[Pd(\eta^3-C_3H_5)]_2$ and $[Me(^tBuN)W(\mu-NBu^t)_2ZnMe(NH_2Bu^t)]$ along with an electron diffraction study of the parent $W(NBu^t)_2(HNBu^t)_2$ [6].

In particular, bi-metallic species involving Group 15 elements are evident by their omission from this list. This may be because, while reaction of $Li_2[W(NBu^t)_4]$ with Group 13 substrates has proved relatively clean [2], the only reported reaction with a Group 15 halide (PCl_3) has proved more complex, yielding $W(NBu^t)Br_2[P_2(NBu^t)_3]$ as the only identifiable product in low (40%) yield [7]; the formal $[P_2(NBu^t)_3]^{2-}$ anion this species incorporates is, however, unique. Our own interest in this general area of heterobimetallic tungsten amides has thus caused us to explore the reaction of $Li_2[W(NBu^t)_4]$ with $SbCl_3$, the results of which are presented herein.

2. Experimental

2.1. General procedures

Elemental analyses were performed using an Exeter Analytical CE 440 analyser. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 300 MHz FT-NMR spectrometer, as a saturated solution at room temperature; chemical shifts are in ppm with respect to Me_4Si, coupling constants are in Hertz.

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology solvent purification system (SPS). $W(NHBu^t)_2(NBu^t)_2$ [4] and $Li_2W(N^tBu)_4$ [2,5] was prepared as described in the literature. $SbCl_3$ was purchased from Aldrich and purified by azeotropic distillation and then by multiple sublimations under vacuum [8].

2.2. Synthesis of $Sb_2W(NBu^t)(\mu_2-NBu^t)(\mu_3-NBu^t)_2Cl_3(\mu_2-Cl)$ (**1**)

A solution of freshly sublimed $SbCl_3$ (0.29 g, 1.3 mmol) in toluene (20 cm^3) was added dropwise to a solution of $Li_2W(N^tBu)_4$ (0.30 g, 0.622 mmol) in toluene (50 cm^3) at $-78\ °C$. On warming to between -20 and $10\ °C$, a white precipitate was formed in the deep yellow solution. After further warming to room temperature, the white solid disappeared to give an orange-red solution. The solution was stirred for 24 h and filtered through Celite. The solution was then concentrated to ca. 3 cm^3 giving rise to an oily solution. Crystallisation from toluene/hexane (1:3) at $-20\ °C$ for 3 days afforded to orange blocks, which were washed with hexane ($3 \times 3\ cm^3$) then dried under vacuum to yield an orange-yellow solid. Yield: 0.13 g, 25%, m.p.: $110\ °C$. *Anal.* Calc. for

$C_{16}H_{36}Cl_4N_4Sb_2W$: C, 22.5; H, 4.2; N, 6.6. Found: C, 22.5; H, 4.4; N, 6.7%. ^1H NMR (C_6D_6, 300 MHz, 298 K, δ ppm): 1.0 (s, 18 H, μ_3-NC$(CH_3)_3$), 1.37 (s, 9H, μ_2-NC$(CH_3)_3$), 1.46 (s, 9H, NC$(CH_3)_3$). ^{13}C NMR (C_6D_6, 300 MHz, 298 K, δ(ppm): 30.0[μ_3-NC$(CH_3)_3$], 31.0 [μ_2-NC$(CH_3)_3$], 34.0 [NC$(CH_3)_3$], 55.9 [μ_3-NC$(CH_3)_3$], 65.0[μ_2-NC$(CH_3)_3$], 75.8 [NC$(CH_3)_3$].

3. Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo Kα radiation (λ = 0.71073 Å). Structure solution followed by full-matrix least squares refinement and was performed using the WINGX-1.70 suite of programmes [9]. Corrections for absorption (multi-scan) were made in all cases. Notes on refinement:

For compound **2**: The asymmetric unit consists of the halves of each of the antimony and tungsten dimers in the co-crystal, which are each located close to an inversion centre. Two out of the three *t*-Bu groups in the tungsten complex show rotational disorder in the ratio 1:1 [atoms C(12)–C(14) and C(32)–C(34)]. Bond lengths and thermal ellipsoids in this disorder were refined using restraints. Atoms H(2A) and H(2B) binding to N(2) were located in the difference Fourier map and freely refined.

For compound **3**: The asymmetric unit contains one complete molecule and 1.5 solvent molecules (Et$_2$O), one of which is located about a centre of inversion. One *t*-Bu group [C(6)–C(8)] is disordered in the ratio 80:20 with some potential disorder in the same ratio in the *t*-Bu group with C(2)–C(4), though it was not possible to resolve this disorder. Bond lengths of C(5)–C(8) and C(5)–C(7A) have been restrained and atoms C(7) and C(8) had to be refined isotropically. H(4) [attached to N(4)] was located in the difference Fourier map but had to be refined with restrained bond length due to its proximity to W(3).

4. Results and discussion

Reaction of Li$_2$[W(NBu^t)$_4$] with two equivalents of freshly sublimed SbCl$_3$ in toluene at −78 °C, followed by warming to room temperature afforded, after separation from LiCl by filtration and
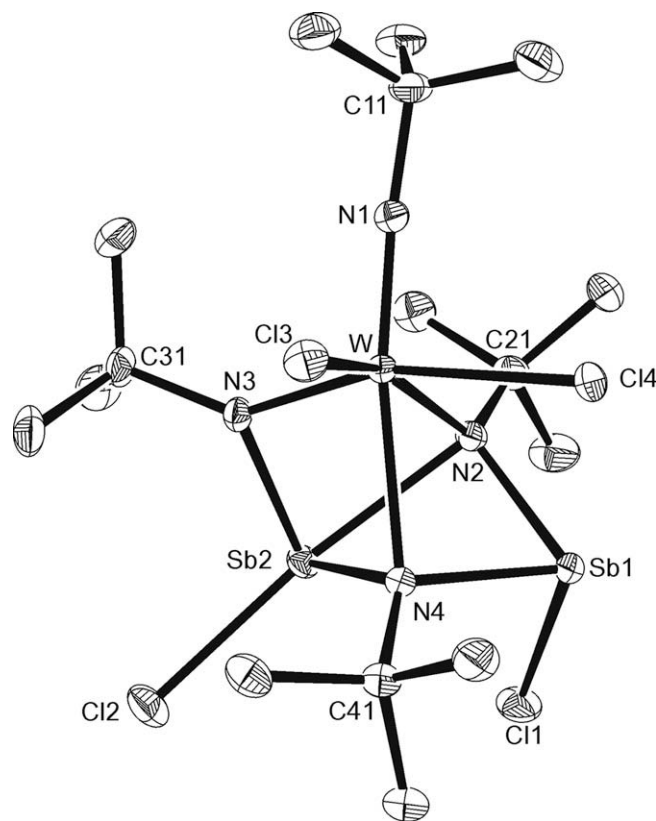

Fig. 1. The asymmetric unit of **1** showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Selected geometric data are given in Table 2.

crystallisation from toluene, orange-red crystals of Sb$_2$W(NBu^t)-(μ_2-NBu^t)(μ_3-NBu^t)$_2$Cl$_3$(μ_2-Cl) (**1**) in low yield (25%):
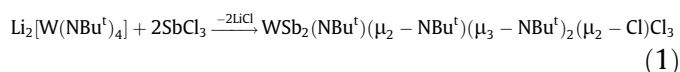
$$Li_2[W(NBu^t)_4] + 2SbCl_3 \xrightarrow{-2LiCl} WSb_2(NBu^t)(\mu_2-NBu^t)(\mu_3-NBu^t)_2(\mu_2-Cl)Cl_3$$

$$(1)$$

Table 1
Crystal data and structure refinement for **1–3**.

	(**1**)	(**2**)	(**3**)
Empirical formula	$C_{16}H_{36}Cl_4N_4Sb_2W$	$C_{16}H_{38}Cl_3N_4SbW$	$C_{60}H_{140}Cl_{14}N_{12}O_9Sb_4W_6$
Formula weight	853.64	698.45	3260.24
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	14.2340(2)	12.5692(3)	12.19420(10)
b (Å)	11.8730(2)	9.7383(2)	12.8309(2)
c (Å)	16.3270(2)	21.0413(5)	18.2983(3)
α (°)			76.314(1)
β (°)	105.292(1)	92.183(1)	85.396(1)
γ (°)			71.837(1)
V (Å^3)	2661.57(7)	2573.64(10)	2643.04(6)
Z	4	4	1
ρ_{calc} (Mg m^{-3})	2.130	1.803	2.048
μ(Mo kα) (mm^{-1})	6.738	5.835	7.903
$F(0\,0\,0)$	1616	1352	1542
Crystal size (mm)	0.40 × 0.30 × 0.15	0.20 × 0.05 × 0.05	0.50 × 0.40 × 0.20
θ (°)	4.42–30.07	3.32–27.50	3.16–25.08
Reflections collected	56 702	26 964	35 200
Independent reflections (R_{int})	7699 (0.0954)	5860 (0.0626)	9308 (0.0468)
Reflections observed (>2σ)	7336	4084	9007
Maximum and minimum transmission	0.4314 and 0.1736	0.7591 and 0.3882	0.3009 and 0.1100
Goodness-of-fit (GOF) on F^2	1.183	1.032	1.191
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0336, 0.0834	0.0487, 0.1149	0.0365, 0.0904
Final R_1, wR_2 (all data)	0.0357, 0.0850	0.0797, 0.1353	0.0388, 0.0917
Largest difference in peak and hole (eÅ^3)	2.334 and −2.932	2.687 and −2.413	2.122 and −2.811