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A New Type of Sulfenamido Ligand. Crystal Structure of $W(NBu^t)_2(\eta^2\text{-PhSNBu}^t)_2$

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The interaction of $Li_2W(NBu^t)_4$ with PhSCl gave $W(NBu^t)_2(\eta^2\text{-PhSNBu}^t)_2$ the structure of which has been determined by X-ray diffraction; reaction of $Li(PhSNBu^t)$ with transition-metal halides allows the synthesis of a range of other compounds with the η^2-N,S ligand.

The interaction of $Li_2W(NBu^t)_4$ with $AlCl_3$ and other Lewis acids gives rise to compounds such as $(Cl_2Al)_2(\mu\text{-NBu}^t)_4W$,[1] whereas the interaction with PX_3 (X = Cl or Br) produced the compounds $W(NBu^t)X_2[P_2(NBu^t)_3]$ having a new type of P–N ligand with W–N bonding.[2] A similar reaction using PhSCl produces a new type of sulfenamide complex, $W(NBu^t)_2(\eta^2\text{-PhSNBu}^t)_2$. Although there has been extensive work[3] on N,S ligands such as RNSNR and $RNS(R')NR^-$ (R = Bu^t or $SiMe_3$; R′ = Bu^t or Ph), including sulfenamides,[4] we are unaware of a ligand of the present type. Noble and co-workers[4] described a bridge, $Mo_2(\mu\text{-SNH}_2)$, while Chivers *et al.*[3] made a series of compounds of the type $M(\eta^5\text{-C}_5H_5)_2Cl(L)$ (M = Ti, Zr or Hf) where L was a ring anion $R_4P_2N_4S_2Me^-$ (R = Me, Bu^t, Ph or CH_2PPh_2) which was η^2-N,S bonded to the metal atom.

The compound $W(NBu^t)_2(\eta^2\text{-PhSNBu}^t)_2$† is a moderately air- and moisture-sensitive crystalline solid the ^1H NMR spectrum of which shows two types of NBu^t resonances in a 1 : 1 ratio. A diagram of the structure, as determined by X-ray diffraction,‡ is shown in Fig. 1. The co-ordination geometry is most conveniently described as distorted bicapped tetrahedral, with the W–N bonds defining the tetrahedron and the rather long W–S bonds, the caps. The imido groups are acting in the usual linear 6e mode, although the W–N bonds are long for interaction with a tungsten(VI) centre. The mode of bonding of the sulfenamide ligand is intriguing. In spite of the long W–S distances, the sulfur would appear to be involved in an interaction with the metal, since the R–N–W angles are much larger than would be expected for simple amido bonding. It is pertinent that whilst the nitrogens are essentially sp^2 planar, the sulfurs are pyramidal, with bond angle sums of 260–264°. We are investigating the nature of the bonding of this type of ligand *via* high-level quantum-mechanical calculations and will report further.

While compounds of this type can be obtained similarly from other $Li_2M(NBu^t)_4$ species, a more useful route is the interaction of metal halides or complex metal halides with $Li(PhSNBu^t)$ or other substituted species. These are obtained by interaction, *e.g.*, of $LiBu^n$ in light petroleum with $PhSN(H)Bu^t$ made from Bu^tNH_2 and PhSCl.[9] Examples of new compounds obtained from the corresponding halides are $MO_2(PhSNBu^t)_2$ (M = Mo or W), $Mo(NBu^t)_2(PhSNBu^t)_2$, $TiCl_2(PhSNBu^t)_2$ and $Zr(\eta^5\text{-C}_5H_5)_2Cl(PhSNBu^t)$. All have been characterised by analyses, spectroscopy and by X-ray crystallography in some cases. Other metal compounds with different sulfenamides and their selenium analogues will be reported later. It may be noted that the $[RENR']^-$ (E = S or Se; R, R′ = allyl or aryl) functionality belongs in the class of α-heteroatom-substituted anionic species such as hydrazido $[RNNR_2']^-$, hydroxylamido $[RNOR']^-$, *etc.*[10]

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† *Synthesis:* to a suspension of $Li_2W(NBu^t)_4$ (0.3 g, 0.63 mmol) in light petroleum (b.p. 40–60 °C) at −78 °C was added dropwise a solution of PhSCl (0.18 g, 1.26 mmol) in light petroleum (30 cm^3). After warming to room temperature (12 h) and filtration, the colourless solution was concentrated (to *ca.* 5 cm^3) and cooled (−20 °C) for 8 h, giving colourless prisms. Yield 0.24 g (*ca.* 55%); m.p. 188–190 °C. NMR(C_6D_6): ^1H, δ 6.9–7.5 (m, 10 H, Ph), 1.48 (s, 18 H, Me_3CN) and 1.27 (s, 18 H, $SNCMe_3$). $^{13}C\text{-}\{^1H\}$, δ 143.2, 129.2, 126.2, 124.5 (aromatic), 67.0 ($NCMe_3$), 61.5 ($SNCMe_3$), 33.7 and 32.3 (CMe_3). Mass spectrum (electron impact): *m/z* 686 (M^+), 671 (*M* − Me), 630 ($M - Me_2C{=}CH_2$) and 615 ($M - NBu^t$).

‡ $C_{28}H_{46}N_4S_2W$, *M* = 686.66, crystal size 0.27 × 0.23 × 0.17 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.510(3)$, $b = 11.051(2)$, $c = 16.051(2)$ Å, $\alpha = 102.39(2)$, $\beta = 96.62(2)$, $\gamma = 117.60(1)°$, $U = 1563(1)$ Å^3, $Z = 2$, $D_c = 1.459$ g cm^{-3}, $\mu = 3.706$ mm^{-1}, $F(000) = 696$. Data were collected at 150 K using a FAST TV area detector diffractometer with Mo-Kα radiation (λ = 0.710 69 Å), as previously described,[5] to give 8434 measured and 7343 unique data. The structure was solved *via* application of the Patterson instruction of SHELXS 86.[6] Refinement was by full-matrix least-squares on F^2 using the program SHELXL 93.[7] The data were corrected for absorption using the program DIFABS[8] with maximum and minimum correction factors of 1.218 and 0.823. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealised positions. The structure was refined to $R_1 = 0.0271$, $wR_2 = 0.0700$ for all data, $R_1 = 0.0245$ for 6409 observed $[I > 2\sigma(I)]$ data, where $R = \Sigma[(F_o) - (F_c)]/\Sigma F_o$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ and $w = 1/[\sigma^2(F_o)^2]$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

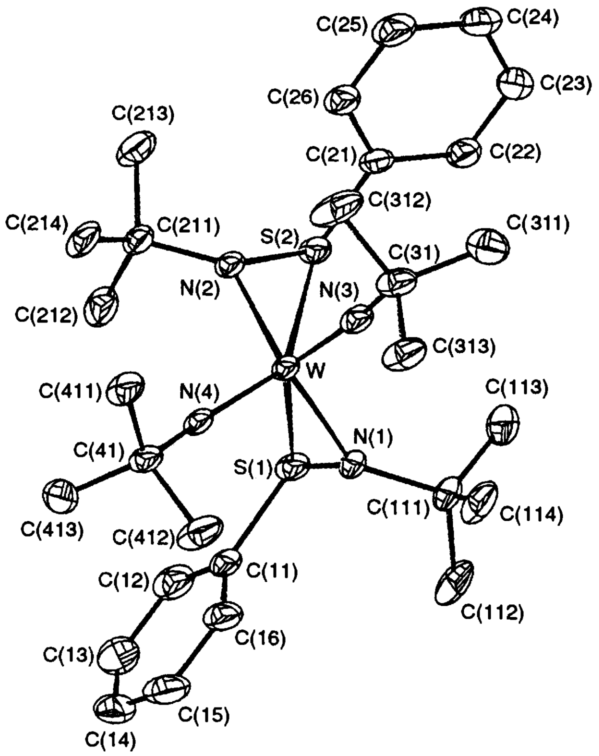

Fig. 1 Molecular structure of W(NBu^t)$_2$(η^2-PhSNBu^t)$_2$. Selected bond lengths (Å) angles (°): W–N(1) 2.017(2), W–N(2) 2.017(2), W–N(3) 1.750(3), W–N(4) 1.760(2), W–S(1) 2.777(1), W–S(2) 2.760(1), S(1)–N(1) 1.681(3), S(2)–N(2) 1.685(2), S(1)–C(11) 1.775(3), S(2)–C(21) 1.776(3), N(1)–C(111) 1.487(3), N(2)–C(211) 1.490(4), N(3)–C(31) 1.448(4) and N(4)–C(41) 1.443(4); N(1)–W–N(2) 123.8(1), N(1)–W–N(3) 107.1(1), N(1)–W–N(4) 104.3(1), N(1)–W–S(1) 36.96(7), N(1)–W–S(2) 93.09(7), N(2)–W–N(3) 104.6(1), N(2)–W–N(4) 106.7(1), N(2)–W–S(1) 91.91(7), N(2)–W–S(2) 37.39(7), N(3)–W–N(4) 110.0(1), N(3)–W–S(1) 139.5(1), N(3)–W–S(2) 97.3(1), N(4)–W–S(1) 99.8(1), N(4)–W–S(2) 141.0(1), S(1)–W–S(2) 73.72(3), C(11)–S(1)–W 112.1(1), C(21)–S(2)–W 108.5(1), C(111)–N(1)–S(1) 118.5(2), C(111)–N(1)–W 136.3(2), C(211)–N(2)–S(2) 119.4(2), C(211)–N(2)–W 135.1(2), C(31)–N(3)–W 164.9(2) and C(41)–N(4)–W 160.6(2)

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