

Illusive tungsten-imido-dithiocarbamate complexes: Facile carbon–nitrogen bond formation

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ARTICLE INFO

Article history:

Received 29 July 2011

Accepted 11 September 2011

Available online 17 September 2011

Keywords:

Tungsten

Imido

Dithiocarbamate

Oxo

Ureato

ABSTRACT

Heating $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$ with a slight excess of ArNCO ($\text{Ar} = \text{Ph}$, *p*-tolyl) results in the rapid formation of imido-ureato complexes $[\text{W}(\text{NAr})\{\kappa^2\text{-ArNC}(\text{O})\text{NAr}\}(\text{S}_2\text{CNBu}^i_2)_2]$, a transformation believed to occur *via* the bis(imido) intermediates $[\text{W}(\text{NAr})_2(\text{S}_2\text{CNBu}^i_2)_2]$. The ureato ligand is easily removed (as the urea) upon addition of gaseous HCl to afford the dichloride $[\text{W}(\text{NAr})\text{Cl}_2(\text{S}_2\text{CNBu}^i_2)_2]$. While bis(imido) complexes are unavailable from the direct reaction of isocyanates (or amines) with $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$, they can be prepared upon addition of dithiocarbamate salts to $[\text{W}(\text{NBu}^t)_2(\text{NHBU}^t)_2]$ addition of two equivalents of $[\text{NH}_2\text{Bu}^i_2][\text{Bu}^i_2\text{NCS}_2]$ affording $[\text{W}(\text{NBu}^t)_2(\text{S}_2\text{CNBu}^i_2)_2]$ in which both imido groups are linear.

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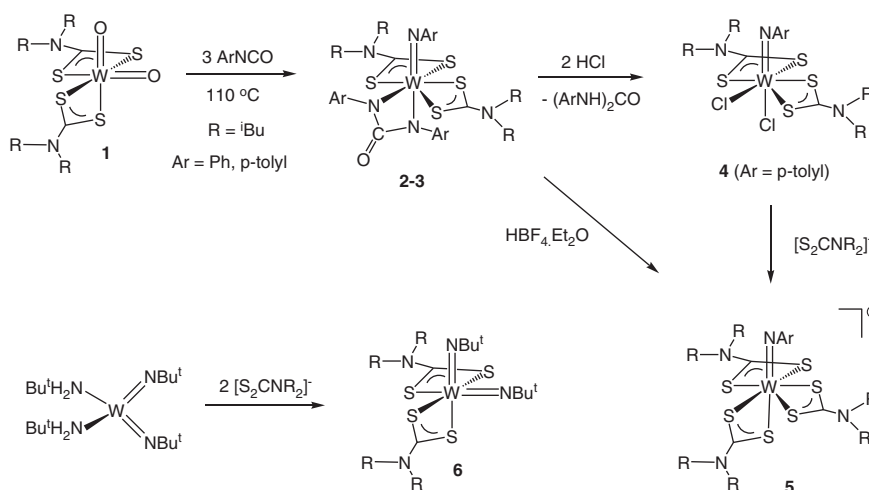
While both tungsten-dithiocarbamate [1] and tungsten-imido [2] chemistry are well developed, somewhat surprising tungsten-imido-dithiocarbamate complexes have to date proved elusive [3]. The precise reason(s) for this are unclear, especially since molybdenum-imido-dithiocarbamate chemistry has been so extensively described [3,4], but a contributing factor is likely the lack of suitable tungsten-oxo-dithiocarbamate precursors since a common route to transition metal imido complexes involves the reactions of metal oxides with primary amines, isocyanates and other imido sources [5]. Young commented on the paucity of tungsten-oxo-dithiocarbamate complexes suggesting that this may be due to their propensity to decompose with formation of the very stable polytungstates [6]. At the time only a few such species were known, including; $[\text{WO}_2(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} = \text{Cy}$, Bz) [7], $[\text{WO}(\text{S}_2\text{CNBz}_2)_2]$ [8] and $[\text{WO}_2\text{Cl}_2(\text{S}_2\text{CNMe}_2)_2]$ [9]. In the intervening 15 years little progress has been made in tungsten-oxo-dithiocarbamate chemistry, with one notable exception. In 2004, Unoura and co-workers reported a relatively simple preparation of the air and moisture stable complex $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$ [10], being formed upon addition of sodium tungstate to an aqueous solution of the dithiocarbamate while carefully regulating the pH. Both the formation and stability of the latter are surprising. Unoura reported that all attempts to make other dithiocarbamate derivatives *via* this simple method failed, while in previously both $[\text{WO}_2(\text{S}_2\text{CNCy}_2)_2]$ [7] and $[\text{WO}_2(\text{S}_2\text{CNBz}_2)_2]$ [8] were reported to be unstable. We were attracted to the potential use of $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$ (1) as a gateway into tungsten-imido-dithiocarbamate chemistry. In particular, we

hoped that reaction with arylisocyanates might lead to CO_2 elimination and formation of the desired imido complexes. We have extensively developed this approach towards the synthesis of molybdenum-imido-dithiocarbamate complexes [11–13], and while the reaction outcomes are not always simple [12,13], in all cases imido-dithiocarbamate complexes result. We were, however, concerned by the report of an early unsuccessful attempt to prepare a tungsten-imido-dithiocarbamate complex upon heating $[\text{WOC}_2(\text{S}_2\text{CNMe}_2)_2]$ with excess PhNCO [9]. The *spectator effect* in multiply bonded ligands is well-documented [14] and we anticipated that the presence of two oxo ligands in $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$ may significantly enhance their reactivity. Indeed this is the case and herein we describe two facile routes into tungsten-imido-dithiocarbamate complexes namely the reaction of ArNCO with $[\text{WO}_2(\text{S}_2\text{CNBu}^i_2)_2]$ which affords ureato complexes and the addition of the dithiocarbamate salt $[\text{NH}_2\text{Bu}^i_2][\text{Bu}^i_2\text{NCS}_2]$ to tungsten bis(*tert*-butylimido) precursors which affords the bis(imido) complex $[\text{W}(\text{NBu}^t)_2(\text{S}_2\text{CNBu}^i_2)_2]$.

Heating a toluene solution of 1 and *ca.* 3 equivalents of ArNCO ($\text{Ar} = \text{Ph}$, *p*-tolyl) in toluene for 1 h results in a marked colour change from pale yellow to bright orange and lead to the isolation of $[\text{W}(\text{NAr})\{\kappa^2\text{-ArNC}(\text{O})\text{NAr}\}(\text{S}_2\text{CNBu}^i_2)_2]$ (2–3) in yields of 30–35% after chromatographic work-up and crystallization from ether (Scheme 1) [15]. The molecular structures of 2–3 were determined [16] and while in both gross structural features were the same, due to a substantial disorder problem in 3 ($\text{Ar} = \text{p}$ -tolyl) only that of $[\text{W}(\text{NPh})\{\kappa^2\text{-PhNC}(\text{O})\text{NPh}\}(\text{S}_2\text{CNBu}^i_2)_2]$ (2) will be discussed (Fig. 1). The coordination geometry about tungsten is an approximate pentagonal bipyramid with the imido ligand and one nitrogen of the ureato ligand, N(5), taking up the axial sites. Such a gross coordination is similar to that found in the cation of the related seven-coordinate complex, $[\text{WS}(\text{S}_2\text{CNET}_3)_3][\text{BF}_4]$ [17];

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Scheme 1. Synthesis of tungsten-imido-dithiocarbamate complexes.

here the sulfide and one sulfur of a dithiocarbamate ligand occupying the axial sites. The imido group displays the classic linear coordination environment [W(1)-N(3)-C(20) 178.7(6)°] and short tungsten–nitrogen interaction [W(1)-N(3) 1.737(7) Å] [5]. The ureato ligand is approximately planar and the phenyl rings lie in this plane. Angles at N(4) and N(5) are close to 360° suggesting that these atoms are sp^2 hybridized. The tungsten–nitrogen bond lengths [W(1)-N(4) 2.077(6) & W(1)-N(5) 2.144(7) Å] vary by only 0.07 Å suggesting that the imido ligand effects only a weak *trans*-influence. The bite-angle at tungsten is small [N(4)-W(1)-N(5) 62.1(3)°] and this leads to a deformation of both nitrogen

atoms from their idealized positions. Thus the angle between the two axial nitrogen atoms is 165.7(3)°, while N(4) is distorted out of the pentagonal plane by 0.595 Å. A hand full of tungsten ureato complexes have previously been reported [18].

In previous work we have noted that addition of arylisocyanate to a bridging imido ligand of the dimeric molybdenum(V) complexes, [Mo(NAr)(S₂CNEt₂)(μ-NAr)]₂, affords a bridging ureato complex *via* a process which is both reversible and regioselective [13]. The latter is a result of the quite asymmetric binding of the ureato ligand to the dimolybdenum centre leading to the suggestion that it is a weakly

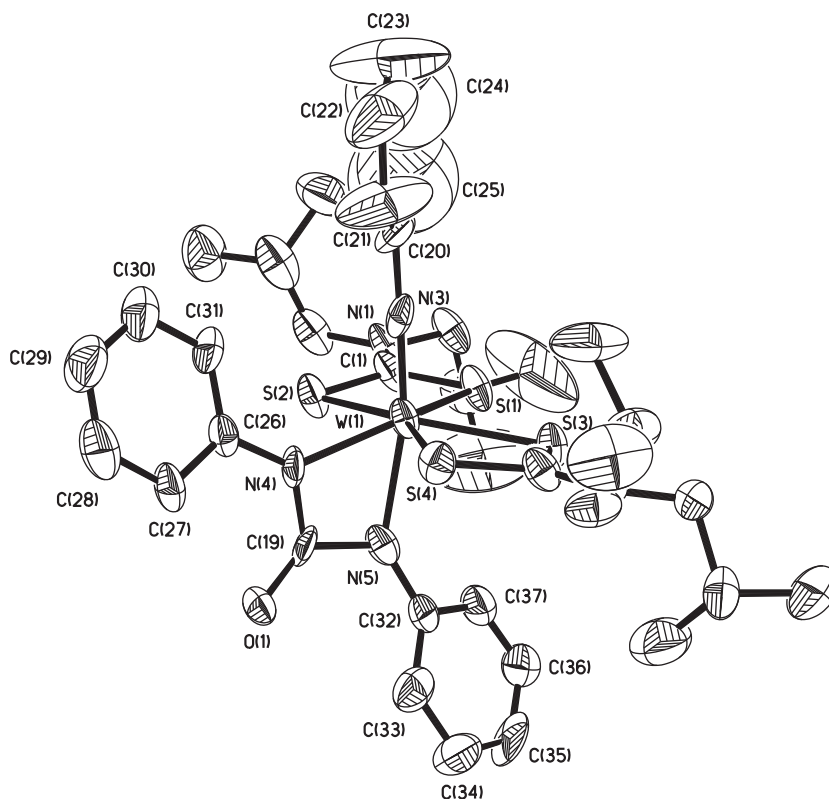


Fig. 1. Molecular structure of [W(NPh){ κ^2 -PhNC(O)NPh}(S₂CNBu₄)₂] (2) with selected bond lengths (Å) and angle (°): W(1)-N(3) 1.737(7), W(1)-N(4) 2.077(6), W(1)-N(5) 2.144(7), W(1)-S(1) 2.521(2), W(1)-S(2) 2.524(2), W(1)-S(3) 2.484(2), W(1)-S(4) 2.535(2), C(19)-O(1) 1.225(10), N(3)-C(20) 1.377(10), N(4)-C(19) 1.349(11), N(5)-C(19) 1.424(10), W(1)-N(3)-C(20) 178.7(6), S(1)-W(1)-S(2) 67.66(7), S(3)-W(1)-S(4) 68.02(7), N(4)-W(1)-N(5) 62.1(3), N(3)-W(1)-N(5) 165.7(3).

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