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## A neutral tungsten-η<sup>2</sup>-alkyne-1-thio ligand forming a homoleptic Werner type complex with Cu(I)<sup>†</sup>

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The 1-thio- $\eta^2$ -alkyne-complex [Tp'(CO)<sub>2</sub>W(BnSCCS)] [Tp' = hydrotris(3,5-dimethylpyrazolyl)borate; Bn = benzyl], which was obtained by reductive removal of the benzyl group at the alkyne complex [Tp'(CO)<sub>2</sub>W(BnSCCSBn)]PF<sub>6</sub>, has been established as a ligand in a combined organometallic/Werner type heterobimetallic complex with Cu(1).

Alkyne-1-thiolato or alkyne-1,2-dithiolato ligands, which can bind one metal centre by the triple bond and the other by coordination through the sulfur donor atoms seem basically promising in order to study cooperative phenomena in heterobimetallic complexes. However, first reports on the coordination chemistry of alkyne-1-thiolato ligands pointed out the tendency of sulfur to govern the complex behaviour even in the formation of dinuclear complexes.1 To the best of our knowledge dinuclear complexes exhibiting an alkyne-1-thiolato-ligand as  $\eta^2$ -CC- $\eta^1$ -S linker between organometallic and Werner type complex centres have not been described so far. Alkyne complexes with a terminal sulfur atom have been synthesized at W(II) and Mo(II) complex centres by coupling of either intermediate carbyne and CS ligands<sup>2</sup> or of carbyne and CO ligands and subsequent reaction with Lawesson's reagent.<sup>3</sup> The  $\eta^2$ -CC-bonding in the resulting complexes is best described by superposition of two resonance forms, underlining either the thioketenyl character (A) or the rather zwitterionic alkyne complex form (B). The nucleophilicity at the sulfur atom, which is particularly evident in form **B**, has not yet been explored with regard to coordination chemistry (Scheme 1).



Scheme 1 Valence bond description of thio-alkyne complexes.

In the course of our studies aimed at generating metal complexes with an alkyne-1,2-dithiolato ligand we found that the thio-alkyne complex [Tp'W(CO)<sub>2</sub>(BnSCCS)] **2** [hereafter Tp' = hydrotris(3,5dimethylpyrazolyl)borate; Bn = C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>] is easily accessible by reductive dealkylation of the corresponding alkyne-1,2-di(thioether) complex [Tp'W(CO)<sub>2</sub>(BnSCCSBn)]PF<sub>6</sub> **1** (Scheme 2).<sup>4</sup> This reactivity is remarkable with regard to the stability of the diphenylalkyne complex [Tp'Mo(CO)<sub>2</sub>(PhCCPh)] obtained by reduction of the corresponding cation.<sup>5</sup> The direct comparison of the C<sub>sp</sub>–S bond lengths of the thioether function and the thione unit in the molecular structure of **2** (Fig. 1) discloses only partial double bond character for the C1–S1 bond applying the bond length criteria.<sup>6</sup> However, the distinctly shorter W–C2 bond [2.012(4)] compared to W–C1 [2.138(4)] is reflected in the resonance form **A**. Variable temperature <sup>1</sup>H NMR investigations with **2** resulted in a free activation enthalpy of 53 kJ mol<sup>-1</sup> of the alkyne rotation between the *syn*- and the *anti*-position of the terminal sulfur regarding the carbonyl ligands. This value is typical for sterically less hindered four-electron W(II) alkyne complexes.<sup>7</sup> In addition, the comparable intensities of the corresponding CH<sub>2</sub> resonances at 213 K exclude a distinct preference for one of the rotational isomers in solution.<sup>‡</sup>



Scheme 2 Reagents: i,  $[Co(C_5H_5)_2]$ ; ii,  $[Cu(CH_3CN)_4]BF_4$ .



Fig. 1 Molecular structure of 2. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles(°): W–C1 2.138(4), W–C2 2.012(4), C1–C2 1.348(6), C1–S1 1.651(5), C2–S2 1.685(4), S1–C1–C2 144.9(4), C1–C2–S2 132.5(4).

In order to investigate the coordination behaviour of **2** we reacted two equivalents of **2** with  $[Cu^{1}(CH_{3}CN)_{4}]BF_{4}$ . Fast complex formation is indicated by the IR shift of the carbonyl stretching frequencies from 2004/1925 cm<sup>-1</sup> for free **2** to 2032/1957 cm<sup>-1</sup>. The perception that  $[Cu(2)_{2}]^{+}$  species (**3a**) exist in solution is based on ES mass (CH<sub>2</sub>Cl<sub>2</sub>) and particularly <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectroscopy, showing primarily one ligand type **2**. However, the solid state molecular structure of  $[Cu_{2}(2)_{4}](BF_{4})_{2}$ , **3b**, consists of centrosymmetrically constrained hexanuclear cations, in which three-coordinated copper centres are linked by two  $\mu_{3}$ -sulfur bridges (Fig. 2). The copper ions are coordinated exclusively by the terminal sulfur centre of **2**, the thioether function does not take part in the coordination. The coordination sphere around the copper centre is best described as distorted T-shaped, because the Cu–S1a and Cu–S1b bonds [2.205(4), 2.182(4) respectively] are significantly shorter than the Cu#–S1a

<sup>†</sup> Electronic supplementary information (ESI) available: NMR spectra of 1, variable temperature NMR spectra and cyclic voltammetry data of 2 and 3a/b. See http://www.rsc.org/suppdata/dt/b4/b404821k/

bond [2.538(4)] and the S1a–Cu–S1b angle [153.64(16)°] is closer to linear than to trigonal. The Cu(1) coordination renders the thioalkyne  $\eta^2$ -CC-bonding at the tungsten centres, compared to free **2**, rather symmetric [Wa–C1a 2.058(14) and Wa–C2a 2.040(15)].§



**Fig. 2** Molecular structure of **3b**. Hydrogen atoms, methyl and phenyl groups are omitted for clarity. Selected bond length (Å) and angles(°): Cu–S1a 2.205(4), Cu–S1b 2.182(4), Cu#–S1a 2.538(4), Wa–C1a 2.058(14), Wa–C2a 2.040(15), C1a–C2a 1.37(2), Wb–C1b 2.073(12), Wb–C2b 2.017(14), C1b–C2b 1.321(8), C1b–S1b 1.677(13), C2b–S2b 1.691(14), S1a–Cu–S1b 153.64(16), Cu#–S1a–Cu 73.25(13), S1a–Cu–S1a# 106.75(13), S1b–C1b–C2b 144.5(12), C1b–C2b–S2b 133.5(11).

Variable temperature <sup>1</sup>H NMR investigations with **3***a*/**b** disclosed a complex dynamic behaviour. The rotation of the alkyne unit at the tungsten centre, which reflects the behaviour of **2**, is now coupled with the likewise fast equilibration between **3a** and its dimer **3b**. However both, **3a** and its rotational isomer, which was found in the solid, clearly overbalance in solution as estimated by the integral ratios. For that, the CH<sub>2</sub> resonance at 3.23 ppm is assigned to the *syn*-position to the pyrazole pocket due to the high field shift and the smaller signals at 5.14 and 5.06 ppm are assigned to the *syn*-position with regard to the CO ligands for the terminal and the bridging ligand **2**, respectively.

Cationic Cu(1) complexes with neutral sulfur donor ligands are normally four-coordinated.8 However, thiourea derivatives and 1-H-pyridinethione ligands, which are related to 2 due to the thiocarbonyl character of the donor centre, form either trigonal planar mononuclear complexes9 or dinuclear complexes with four-coordinated Cu centres through the linkage of two [CuL<sub>3</sub>] units by two  $\mu_3$ -S bridges.<sup>10</sup> In contrast, mononuclear two-coordinated [Cu(I)L<sub>2</sub>] complexes have been described with either sterically demanding thiolato or thiocarboxylato ligands.11 The Cu-S bond distances in these anionic complexes [2.14, 2.15 Å]11 are shorter than those in cationic complexes with neutral sulfur ligands [2.24 to 2.36 Å].8-10 Two thoroughgoing resonance forms of 3a can be drawn, either emphasizing a cationic copper centre with resonance form A or entailing a rather anionic complex core based on **B**. The change of the CO stretching frequencies from 2 to 3a indicates the shift of positive charge to the tungsten centres in 3a. Considering the Cu-S bond lengths and the coordination numbers the bonding of 2 with Cu(1) in the cationic complex 3b ranges between neutral thiourea derivatives and anionic thiolate ligands. This observation can be attributed to the specific donor ability of 2, which is based on its electronic flexibility. One comparable example of a two-coordinated Cu(1) complex with a metallo-dithiocarbamoyl-ligand showing short Cu–S bonds [2.164 Å] has been published very recently.<sup>12</sup>

Cyclic voltammetry provided insights into the redox responsivity of **2** for complexation to Cu(1) in **3a**. The CV of **2** in CH<sub>2</sub>Cl<sub>2</sub> shows a reversible reduction wave at -1.69 V (peak potential referenced *vs*. Fc/Fc<sup>+</sup> hereafter), which is only marginally shifted in the heterobimetallic complex **3a**. This can be rationalized by the observation of an irreversible reduction wave at -1.3 V, which is assigned to Cu(1)/Cu(0) by comparison with [Cu{SC(NMe<sub>2</sub>)<sub>2</sub>}<sub>3</sub>]. However in contrast to **2**, which is irreversibly oxidized at approx. 0.4 V, **3a** undergoes two positively shifted but still irreversible oxidations at 0.6 and 0.8 V, which are difficult to assign unequivocally.

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## Note and references

<sup>‡</sup> Selected spectral data for the complexes: satisfactory elemental microanalyses for **1**, **2** and **3b** have been obtained; **1**: green crystals, yield 67%; IR (KBr): ν(CO) 2041, 1980 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) <sup>1</sup>H: δ 4.87, 3.11 (s, 2 H, SCH<sub>2</sub>); <sup>13</sup>C: δ 219.0 (<sup>1</sup>J<sub>WC</sub> = 50 Hz), 193.6 (WCC), 213.8 (<sup>1</sup>J<sub>WC</sub> = 137 Hz, WCO), 43.8, 41.8 (SCH<sub>2</sub>); **2**: brown crystals, yield 48%; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2004, 1925 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>, two isomers) <sup>1</sup>H (213 K): δ 5.25 (s, 48% CH<sub>2</sub>), 3.22 (s, 52% CH<sub>2</sub>); <sup>13</sup>C (213 K): δ 237.6, 232.7 (WCSCH<sub>2</sub>), 220.7, 219.3 (WCO), 214.3, 213.8 (WCS), 40.0, 36.4 (SCH<sub>2</sub>); **3b**: red crystals, yield 53%; IR (**3a**/b, CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2032, 1957 cm<sup>-1</sup>; NMR (**3a**/b, CDCl<sub>3</sub>, 243 K) <sup>1</sup>H: δ 5.14 (s, 4% SCH<sub>2</sub>), 5.06 (s, 15% SCH<sub>2</sub>), 3.23 (s, 81% SCH<sub>2</sub>); I<sup>3</sup>C (major isomer): δ 229.0, 213.7 (WCC), 216.9 (WCO), 40.9 (SCH<sub>2</sub>); ES-MS (CH<sub>2</sub>Cl<sub>2</sub>): m/z (%) 1496 (100, correct isotopic pattern).

§ Crystal data: 2·C<sub>7</sub>H<sub>8</sub>: C<sub>33</sub>H<sub>37</sub>BN<sub>6</sub>O<sub>2</sub>S<sub>2</sub>W, *M* = 808.47; triclinic, space group *P*-1, *a* = 9.9295(6), *b* = 11.7792(7), *c* = 15.1729(9) Å, *a* = 88.117(1),  $\beta$  = 78.308(1),  $\gamma$  = 79.040(1)°, *U* = 1706.10(18) Å<sup>3</sup>, *D<sub>c</sub>* = 1.574 g cm<sup>-3</sup>,  $\lambda$  = 0.71073 Å,  $\mu$  = 3.547 mm<sup>-1</sup>, *T* = 153 K, 1.37 <  $\theta$  < 25°, *R*1 = 0.031 [*I* > 2 $\sigma$ (*I*)], GOF = 1.025. **3b**·2 C<sub>4</sub>H<sub>10</sub>O: C<sub>112</sub>H<sub>132</sub>B<sub>6</sub>Cu<sub>2</sub>F<sub>8</sub>N<sub>24</sub>O<sub>10</sub>S<sub>8</sub>W<sub>4</sub>, *M* = 3310.24; triclinic, space group *P*-1, *a* = 11.008(4), *b* = 17.579(7), *c* = 19.295(8) Å, *a* = 65.382(7),  $\beta$  = 78.082(8),  $\gamma$  = 89.510(8°, *U* = 3309(2) Å<sup>3</sup>, *D<sub>c</sub>* = 1.661 g cm<sup>-3</sup>,  $\lambda$  = 0.71073 Å,  $\mu$  = 3.978 mm<sup>-1</sup>, *T* = 153 K, 1.90 <  $\theta$  < 25.17°, *R*1 = 0.0783 [*I* > 2 $\sigma$ (*I*)], GOF = 1.027. CCDC reference numbers 223069 (**2**·C<sub>7</sub>H<sub>8</sub>) and 223070 (**3b**·2 C<sub>4</sub>H<sub>10</sub>O). See http://www.rsc.org/suppdata/dt/b4/b404821k/ for crystallographic data in CIF or other electronic format.

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