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[3 + 2] Cycloaddition reactions of the phospha-alkyne, Bu^tCP, with a transition metal trisulphide containing terminal thio ligands: syntheses, crystal and molecular structures of $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2PC^tBu)]_2$ and $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2C_2Ph_2)]_2$

Sarah E. d'Arbeloff [a], Peter B. Hitchcock [a], John F. Nixon [a,*], Takayuki Nagasawa [b], Hiroyuki Kawaguchi [b], Kazuyuki Tatsumi [b]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, Sussex, UK*

[b] *Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan*

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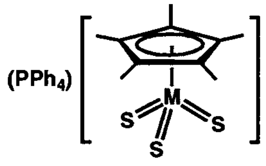
Abstract

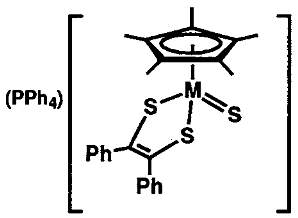
The trisulphido complex $[PPh_4][W(\eta^5\text{-}(C_5Me_5)(S)_3]$, reacts with the phospha-alkyne Bu^tCP and O_2 to afford the dimeric complex $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2PC^tBu)]_2$. Analogous reactions occur with the alkyne Ph_2C_2 to give $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2C_2Ph_2)]_2$. The molecular structures of both complexes are presented and discussed.

Keywords: Cycloaddition; Thio ligands; Trisulfide

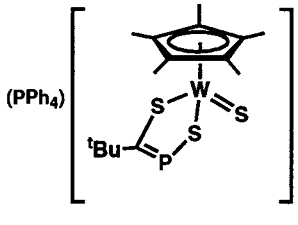
There is considerable current interest in the study of metal sulphides, in view of their biological importance and their potential in the design of new materials [1,2]. The reactivity of certain transition metal sulphides towards alkenes [3] and alkynes [4,5] has been discussed, but a very recent report by Goodman and Rauchfuss [6], which describes the addition of nitriles to the tetrasulphido anion $[ReS_4]^-$, prompts us to report the first example of the ready addition of the phospha-alkyne, Bu^tCP, **1**, to the anionic mononuclear trisulphido complex $[PPh_4][W(\eta^5\text{-}(C_5Me_5)(S)_3]$ **2**, containing three terminal W=S bonds.



2, M = W
3, M = Mo



4, M = W
5, M = Mo



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[*] Corresponding author. Tel.: + 44 273 678536; fax: + 44 273 677196; e-mail: j.nixon@sussex.ac.uk

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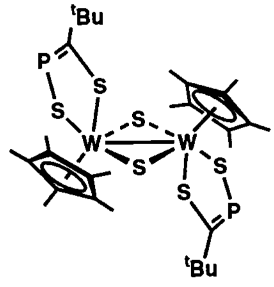

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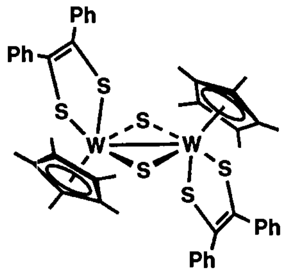

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Previously [7,8], we showed that the addition of the alkyne Ph_2C_2 to complex **2** and its molybdenum analogue **3**, afforded mononuclear complexes **4** (M = W) and **5** (M = Mo), respectively, which were both fully characterised.

In view of the well-known similarity in behaviour of alkynes and phospha-alkynes towards transition metals [9–12] and the previously reported synthesis of several five-membered heterocyclic compounds by [3 + 2] cycloaddition reactions involving phospha-alkynes, it was of interest to study the reaction of the anionic trisulphide complex **2** with the phospha-alkyne Bu^{t}CP. Monitoring the r.t. reaction between **2** and one equivalent of Bu^{t}CP in acetonitrile by ^{31}P-NMR spectroscopy, showed the rapid development of a new signal ($\delta_P = 210.3$ ppm) assigned to complex **6**, which has not yet been possible to isolate. The same complex is obtained in the presence of five equivalents of Bu^{t}CP.

However, when dry O_2 was passed through a solution of **6**, the green–brown complex $[W(\eta^5\text{-}(C_5Me_5)(S)(S_2PC^tBu)]_2$ **7** was readily formed and isolated, ($\delta_P = 101.4$ ppm, $^2J(WP) = 26.8$ Hz) (52%) [13]. A single crystal X-ray diffraction study of the CH_2Cl_2 solvate, revealed the dimeric structure shown in Fig. 1 [14].

In a similar way, the green solution of **4** reacted with dioxygen, instantly turning purple. The purple intermediate has not yet been characterised but it seems to be paramagnetic. After 1 day at r.t., the colour of the solution gradually changed to green and deposited crystals (41%) of the dark-green dimeric complex **8** [15], whose structure, also determined by a single crystal X-ray diffraction study, is shown in Fig. 2 [16].

The close similarity in the structures of **7** and **8** is self-evident from an inspection of the bond length and bond angle data summarised in Figs. 1 and 2. The W···W, W–S and W=S distances in the two complexes are identical within experimental error. The WS_2PC and WS_2C_2 ring systems are planar in **7** and **8**, respectively. This could be interpreted as involving some π-delocalisation as expected for 1,2-phospha-ene thiolato and 1,2-enethiolato coordination; however the C(1)–P distance, 1.66(2) Å in **7**, and the C(11)–C(18) distance, 1.358(5) Å in **8**, are consistent with localised P=C and C=C double bonds, respectively.

The ready [3 + 2] cycloaddition reaction of these anionic trithio complexes with phospha-alkynes, suggests that other metal sulphides containing terminal M=S bonds may also form this type of compound. Complex **6** also readily reacts with metal carbonyl compounds, in the presence of an excess of Bu^{t}CP, to give the cage compound $P_2C_2Bu^t_2CO$, (previously obtained by Cowley et al. [17] from the reaction of Bu^{t}CP and $[Ti(\eta^5\text{-}(C_5H_5)(CO)_2])$, and a mixture of the 1,2,4- and 1,3,4-thiadiphospholes $P_2SC_2Bu^t_2$. The 1,2,4-thiadiphosphole was first reported by Lindner et al. [18] in an unusual reaction involving Bu^{t}CP and η^2-thiophosphinato cobalt and manganese complexes, but the 1,3,4-isomer has not been previously reported, and it will be the subject of a separate publication [19].

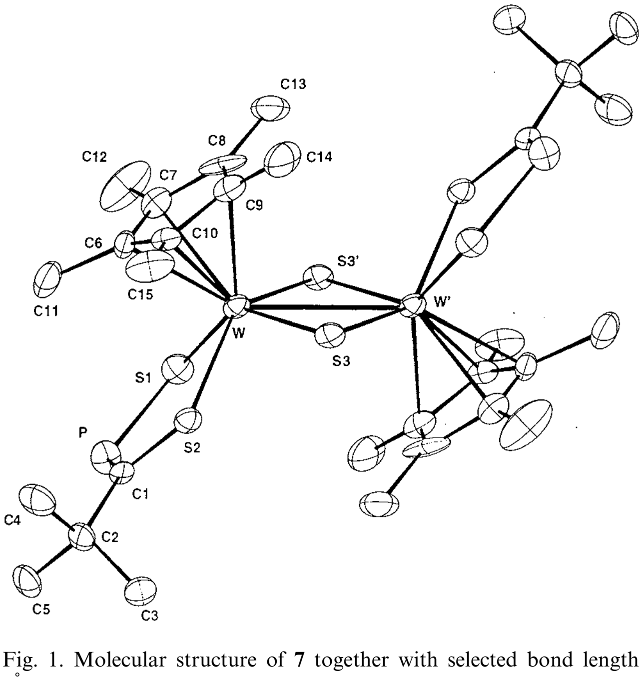

Fig. 1. Molecular structure of **7** together with selected bond length (Å) and bond angle (°) data: W···W 3.068(2), W–S(1) 2.404(6), W–S(2) 2.403(4), W–S(3) 2.337(5), W–S(3)' 2.324(5), S(1)–P 2.039(7), S(2)–C(1) 1.74(2), C(1)–P 1.66(2); W–S(3)–W 82.3(2), S(2)–W–S(1) 79.9(2), W–S(2)–C(1) 116.1(6), W–S(1)–P 116.3(3), S(2)–C(1)–P 122.4(9), S(1)–P–C(1) 102.8(7).

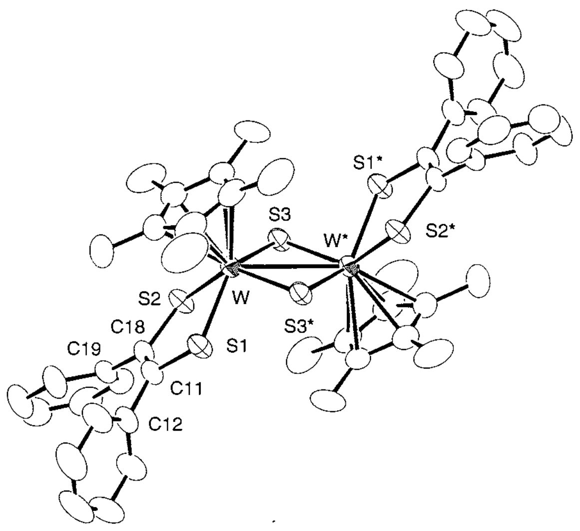

Fig. 2. Molecular structure of **8** together with selected bond length (Å) and bond angle (°) data: W···W 3.0652(3), W–S(1) 2.402(1), W–S(2) 2.401(1), W–S(3) 2.348(1), W–S(3)* 2.344(1), S(1)–C(11) 1.736(4), S(2)–C(18) 1.740(4), C(11)–C(18) 1.358(5); W–S(3)–W* 81.58(3), S(2)–W–S(1) 78.07(3), W–S(2)–C(18) 111.3(1), W–S(1)–C(11) 111.1(1), S(2)–C(18)–C(11) 118.3(3), S(1)–C(11)–C(18) 118.9(3).

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[13] **7**: ^{1}H-NMR (360 MHz, CD_3CN); δ 1.82 (s, C_5Me_5, 30H), 0.61 (s, Bu^t, 18H).

[14] Crystal data for **7**: $C_{31}H_{50}Cl_2P_2S_6W_2$, $M = 1115.6$, monoclinic, space group $C2/c$ (No. 15), $a = 28.794(6)$, $b = 9.435(6)$, $c = 15.074(4)$ Å, $\beta = 107.17(2)^\circ$, $U = 3913(3)$ Å^3, $Z = 4$, $D_{calc} = 1.89$ g cm^{-3}, $F(000) = 2716$. Monochromated Mo–K$_\alpha$ radiation $\lambda = 0.71073$ Å, $T = 173(2)$ K. Data were collected on an Enraf-Nonius CAD 4 diffractometer using a crystal of $0.20 \times 0.20 \times 0.05$ mm. A total of 3423 independent reflections were measured for $2 < \theta < 25^\circ$ of which 2165 had $I > 2\sigma I$. The structure was solved by direct methods using SHELXS-86 and refined on F^2 with all non-H atoms anisotropic using SHELXL-93. Methyl-H atoms were included in riding mode, fixed at idealised geometry, but with the torsional angle defining the H atom positions refined and $U_{iso}(H) = 1.5U_{eq}(C)$. The final residues were $R_1 = 0.075$ (for $I > 2\sigma I$) and $wR_2 = 0.203$ for all data.

[15] **8**: ^{1}H-NMR (500 MHz, $CDCl_3$); δ 2.02 (s, C_5Me_5, 30H), 7.2 (m, Ph, 20H). UV-visible (λ_{max}, nm THF): 409, 542, 638. Found C, 49.01, H, 4.41, S, 15.89; $C_{48}H_{50}W_2S_6$ requires C, 48.57, H, 4.25, S, 16.21%.

[16] Crystal data for **8**: $C_{48}H_{50}S_6W_2$, $M = 1186.98$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.5450(9)$, $b = 11.1888(8)$, $c = 9.898(1)$ Å, $\alpha = 96.359(8)$, $\beta = 91.321(8)$, $\gamma = 77.343(6)^\circ$, $U = 1132.4(2)$ Å^3, $Z = 1$, $D_{calc} = 1.740$ g cm^{-3}, $F(000) = 582.00$. Monochromated Mo–K$_\alpha$ radiation $\lambda = 0.71069$ Å, $T = 296$ K. Data were collected on a Rigaku AFC7R diffractometer using a crystal of $0.20 \times 0.25 \times 0.15$ mm. A total of 5203 independent reflections were measured for $2 < \theta < 25^\circ$ of which 4430 had $I > 3\sigma I$. The structure was solved by Patterson methods and refined by full-matrix least-squares with all non-H atoms anisotropic using the TEXSAN package. The final residues were $R = 0.023$ and $R_w = 0.027$ (for $I > 3\sigma I$).

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