A Trinuclear Cluster Containing a Terminally Bound Alkyne Ligand: Synthesis and *X*-Ray Crystal Structure of [$Co_2W(\mu$-$S)(\mu$-$SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)$]

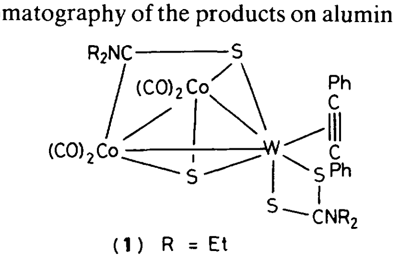
John C. Jeffery[a] **and Michael J. Went***[b]

[a] *Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.*
[b] *University Chemical Laboratory, Canterbury, Kent CT2 7NH, U.K.*

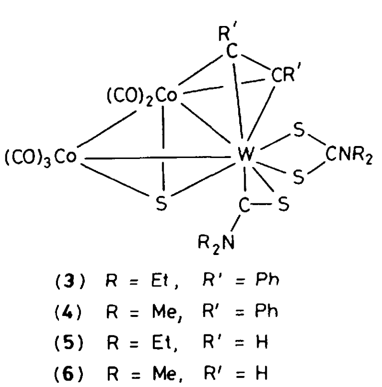
Reaction of [$W(CO)(C_2Ph_2)(S_2CNEt_2)_2$] with [$Co_2(CO)_8$] affords the complex [$Co_2W(\mu$-$S)(\mu$-$SCNEt_2)(CO)_4(C_2Ph_2)$-($S_2CNEt_2$)], the structure of which has been established by *X*-ray diffraction.

Reactions between alkynes and transition metal cluster compounds have been extensively investigated and have led to the identification of a variety of alkyne co-ordination modes.[1—3] The propensity for alkynes to bridge metal–metal bonds is reflected in a dearth of terminally co-ordinated alkyne ligands in polynuclear systems.[4] Indeed, no examples of cluster complexes containing an alkyne bound to a single metal centre have previously been reported.[3]

Our investigations into the ability of mononuclear alkyne complexes to act as cluster precursors have shown that the complex [$W(CO)(C_2Et_2)_3$], containing alkyne ligands formally donating $3\frac{1}{3}$ electrons to the tungsten centre, reacts with [$Co_2(CO)_8$] to form a trinuclear cluster.[5] In order to determine whether a 4 electron donor alkyne system would act in a similar manner, an equimolar mixture of [$W(CO)(C_2Ph_2)$-($S_2CNEt_2)_2$][6] and [$Co_2(CO)_8$] was stirred in dichloromethane for 2 h. Chromatography of the products on alumina separates the purple species (**1**) and brown (**3**).† The molecular structure of (**1**) has been established by a single crystal *X*-ray diffraction study and is shown in Figure 1.‡ The dicobalt–tungsten



(**1**) R = Et
(**2**) R = Me



(**3**) R = Et, R' = Ph
(**4**) R = Me, R' = Ph
(**5**) R = Et, R' = H
(**6**) R = Me, R' = H

---

† *Selected spectroscopic data:* Compound (**1**), ν_{CO} (toluene) 2020s, 1987vs, 1961m, and 1940w cm^{-1}; n.m.r.: ^1H ($CDCl_3$), δ 8.40—7.20 (m, 10H, Ph), 4.28—4.00 (m, 4H, CH_2), 3.73—3.62 (m, 1H, CH_2), 3.48—3.29 (m, 3H, CH_2), 1.47 [t, 3H, CH_3, *J*(HH) 7 Hz], 1.33 [t, 3H, CH_3, *J*(HH) 7 Hz], 1.09 [t, 3H, CH_3, *J*(HH) 7 Hz], and 1.08 [t, 3H, CH_3, *J*(HH) 7 Hz]; $^{13}C\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), 233 K, δ 227.5 (s, $SCNEt_2$), 202.0 (s, CPh), 201.1 (s, S_2CNEt_2), 199.9 (s, CPh), 197.5 (s, CO), 194.8 (s, CO), 138.2, 135.8 (2 × s, *ipso*-C), 130.7, 129.9 (2 × s, *m*-C), 129.2, 129.0 (2 × s, *p*-C), 128.1, 127.8 (2 × s, *o*-C), 51.2, 49.3, 44.4, 44.3 (4 × s, CH_2), and 12.7, 12.0, 11.5, 11.1 (4 × s, CH_3).

Compound (**3**), ν_{CO} (light petroleum) 2058s, 2014s, 1997m, and 1978w cm^{-1}; n.m.r.: $^{13}C\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 244.7 [s, $SCNEt_2$, *J*(WC) 81 Hz], 212.7 (s, CO), 211.2 (s, CO), 205.7 (s, S_2CNEt_2), 199.4 (s, CO), 141.8—123.7 (C_2Ph_2), 52.6—44.1 (CH_2), and 15.7—11.8 (CH_3).

Compound (**5**), ν_{CO} (light petroleum) 2060s, 2015vs, 1966m, and 1972w cm^{-1}; n.m.r.: ^1H (CD_2Cl_2), δ 8.27 (s, 1H, CH), 6.62 (s, 1H, CH), 4.1—3.4 (m, 8H, CH_2), 1.40 [t, 3H, CH_3, *J*(HH) 7 Hz], 1.28 [t, 3H, CH_3, *J*(HH) 7 Hz], 1.25 [t, 3H, CH_3, *J*(HH) 7 Hz], and 1.05 [t, 3H, CH_3, *J*(HH) 7 Hz]; $^{13}C\{^1H\}$ (CD_2Cl_2–CH_2Cl_2), δ 247.2 [s, $SCNEt_2$, *J*(WC) 79 Hz], 211.5 (s, CO), 206.5 (s, S_2CNEt_2), 199.0 (s, CO), 112.4 [s, CH, *J*(WC) 16 Hz], 108.3 [s, CH, *J*(WC) 28 Hz], 52.3, 45.1, 44.3 (3 × s, CH_2), and 15.5, 12.8, 12.7, 12.2 (4 × s, CH_3).

Compound (**6**), ν_{CO} (diethyl ether) 2057s, 2013vs, 1994s, and 1966w cm^{-1}; n.m.r.: ^1H (CD_2Cl_2), δ 8.30 (s, 1H, CH), 6.82 (s, 1H, CH), 3.70 (s, 3H, CH_3), 3.60 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), and 3.16 (s, 3H, CH_3); $^{13}C\{^1H\}$ (CD_2Cl_2), δ 249.2 (s, $SCNMe_2$), 211.2 (s, CO), 207.8 (s, S_2CNMe_2), 198.7 (s, CO), 113.3 (s, CH), 107.9 [s, CH, *J*(WC) 29 Hz], and 49.1, 47.2, 39.8, 39.0 (4 × s, CH_3).

‡ *Crystal data* for (**1**): $C_{28}H_{30}Co_2N_2O_4S_4W$, $M = 888.5$, monoclinic, space group $P2_1/c$, $a = 10.798(4)$, $b = 17.658(4)$, $c = 18.421(6)$ Å, $\beta = 103.88(3)°$, $U = 3410(2)$ Å^3, $Z = 4$, $D_c = 1.73$ g cm^{-3}, $F(000) = 1744$, $\mu(\text{Mo-}K_\alpha) = 46.7$ cm^{-1}, $R = 0.031$ ($R_w = 0.032$) for 4611 unique absorption-corrected intensities [293 K, Wyckoff ω-scans, $4 \leqslant 2\theta \leqslant 50°$, $I \geqslant 2.5\sigma(I)$, Mo-K_α *X*-radiation ($\bar{\lambda} = 0.710\,69$ Å)]. Data were collected on a Nicolet *P3m* diffractometer and the structure was solved by Patterson and Fourier methods with blocked-cascade least-squares refinement.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

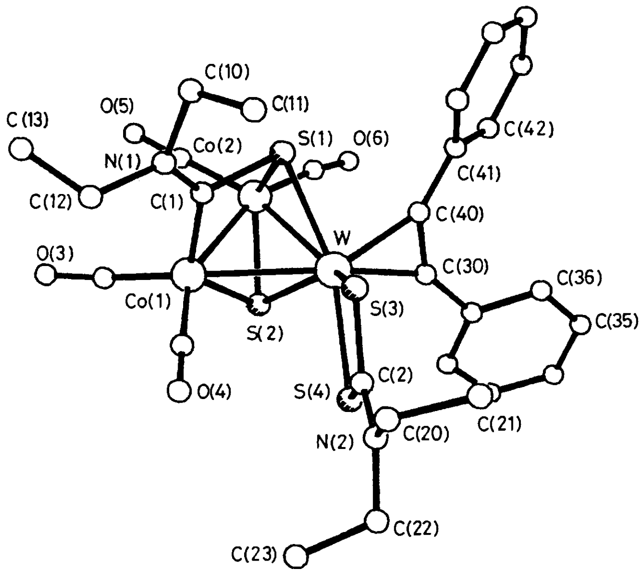


Figure 1. Molecular structure of $[Co_2W(\mu\text{-}S)(\mu\text{-}SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)]$ (**1**). Dimensions W–Co(1) 2.701(1), W–Co(2) 2.601(1), W–S(1) 2.450(1), W–S(2) 2.343(2), W–S(3) 2.454(2), W–S(4) 2.512(1), W–C(30) 2.034(5), W–C(40) 2.044(5), Co(1)–Co(2) 2.492(1), Co(1)–S(2) 2.210(2), Co(1)–C(1) 1.900(6), Co(2)–S(1) 2.239(2), Co(2)–S(2) 2.190(2), S(1)–C(1) 1.772(6), S(3)–C(2) 1.745(6), S(4)–C(2) 1.714(7), C(1)–N(1) 1.314(8), C(2)–N(2) 1.308(8), C(30)–C(40) 1.316(8) Å; Co(1)–W–Co(2) 56.0(1), W–Co(1)–Co(2) 60.0(1), W–Co(2)–Co(1) 64.0(1)°.

triangle is capped on opposite sides by sulphido and thiocarboxamido ligands formed by cleavage of one of the dithiocarbamate groups.[7] The tungsten centre is also ligated by the remaining dithiocarbamate ligand and the terminally bound diphenylacetylene. The bond lengths W–C(40) [2.044(5) Å] and W–C(30) [2.034(5) Å] compare well with the average tungsten–carbon bond length in $[W(CO)(C_2H_2)(S_2CNEt_2)_2]$ (2.03 ± 0.01 Å) and indicate that the alkyne is acting as a 4 electron donor.[8] This leads to a formal cluster valence electron count of 48 as expected for a triangular cluster.[9] The nature of the alkyne bonding is confirmed by the $^{13}C\{^1H\}$ n.m.r. spectrum. At 233 K signals are observed at δ 202.0 and 199.9 corresponding to alkyne carbons in positions typical for a 4 electron donor interaction.[10] Upon warming to room temperature the alkyne resonances coalesce, whilst the other resonances remain distinct, indicating alkyne rotation.

Upon standing in solution for *ca.* 48 h, compound (**3**) is cleanly converted into (**1**), as monitored by a shift of the carbonyl i.r. absorptions to lower frequencies by *ca.* 34 cm^{-1}, precluding detailed analysis of (**3**). Although similar behaviour is observed for the dimethyldithiocarbamate derivatives (**2**) and (**4**), use of $[W(CO)(C_2H_2)(S_2CNR_2)_2]$ results in analogous brown compounds [R = Et, (**5**); R = Me, (**6**)] which are not converted into purple products. N.m.r. spectroscopy reveals that the brown complexes (**3**)—(**6**) do not contain terminally bound 4 electron donor alkyne ligands. For example, ^1H n.m.r. resonances for the acetylene ligand in (**5**) occur at δ 8.27 and 6.62, whilst the corresponding ^{13}C resonances occur at δ 112.4 and 108.3. Although these chemical shifts do not clearly distinguish between an alkyne terminally bound as a 2 electron donor or co-ordinated in a bridging mode, the static nature of the alkyne suggests a bridging interaction as is observed in $[Mo_2(\mu\text{-}S)(\mu\text{-}C_2Et_2)(S_2CNMe_2)_3(SCNMe_2)]$.[11] A resonance at δ 247.2 is assigned to the thiocarboxamido ligand and can be compared to that of δ 257.5 found in $[W(S)(C_2Ph_2)(S_2CNEt_2)(SCNEt_2)]$.[12] In contrast with (**1**) and (**2**), the thiocarboxamido carbon is ligated to the tungsten centre as revealed by ^{183}W satellite peaks [*J*(WC) 79 Hz]. The carbonyl resonances are broad indicating ligation to cobalt and the illustrated structure containing one more carbonyl ligand than (**1**) and (**2**) is proposed on the basis of the spectroscopic data.

It is evident that the alkyne ligands are intimately involved in the process of cluster building despite their formally 4 electron donor interaction in the starting materials $[W(CO)(alkyne)(S_2CNR_2)_2]$. This point is reinforced by the observation that $[W(CO)_3(S_2CNEt_2)_2]$ does not react with $[Co_2(CO)_8]$.

Received, 14th July 1987; Com. 1023

References

1 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323.
2 E. Sappa, A. Tiripicchio, and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
3 P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 170.
4 J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1581.
5 L. J. Farrugia and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1987, 973.
6 B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, 1980, **102**, 1532.
7 D. C. Brower, T. L. Tonker, J. R. Morrow, D. S. Rivers, and J. L. Templeton, *Organometallics*, 1986, **5**, 1093, and references therein.
8 L. Ricard, R. Weiss, W. E. Newton, G. J.-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, 1978, **100**, 1318.
9 J. W. Lauher, *J. Am. Chem. Soc.*, 1978, **100**, 5305.
10 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.
11 R. S. Herrick, S. J. Nieter-Burgmayer, and J. L. Templeton, *J. Am. Chem. Soc.*, 1983, **105**, 745.
12 J. R. Morrow, T. L. Tonker, and J. L. Templeton, *J. Am. Chem. Soc.*, 1983, **105**, 2599.