Heteronuclear Transition Metal-Alkyne Clusters. Part 2.[1] Formation of Trinuclear Clusters *via* Reactions of $[W(CO)(R^1C_2R^2)(S_2CNR_2)_2]$ ($R^1 = R^2 = Ph$ or H, R = Me or Et; $R^1 = R^2 = R = Me$; $R^1 = Ph$, $R^2 = H$, R = Et) with Octacarbonyldicobalt. *X*-Ray Crystal Structure of $[WCo_2(\mu\text{-}S)(\mu\text{-}SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)]$†

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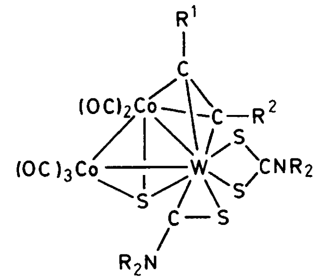
Reactions between $[W(CO)(R^1C_2R^2)(S_2CNR_2)_2]$ ($R^1 = R^2 = Ph$ or H, R = Me or Et; $R^1 = R^2 = R = Me$; $R^1 = Ph$, $R^2 = H$, R = Et) and $[Co_2(CO)_8]$ afford the trinuclear metal complexes $[WCo_2(\mu\text{-}R^1C_2R^2)(\mu\text{-}S)(CO)_5(SCNR_2)(S_2CNR_2)]$ which have been characterised by analytical and spectroscopic methods. All the compounds, except the ethyne derivatives, undergo carbonyl loss and rearrangement in solution to afford $[WCo_2(\mu\text{-}S)(\mu\text{-}SCNR_2)(CO)_4(R^1C_2R^2)(S_2CNR_2)]$. The molecular structure of $[WCo_2(\mu\text{-}S)(\mu\text{-}SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)]$ has been established by an *X*-ray diffraction study. The cluster has a triangular metal framework [W-Co 2.701 (1) and 2.601 (1) Å, Co-Co 2.492(1) Å] which is bicapped by the sulphido and thiocarboxamido ligands. The cobalt atoms are each ligated by two terminal carbonyl groups, while the tungsten atom is co-ordinated by a diethyldithiocarbamato ligand and a non-bridging diphenylacetylene ligand. Carbon-13 n.m.r. spectroscopic studies confirm that the alkyne is acting as a four-electron donor and undergoes a fluxional process in solution which averages the two ends of the bound alkyne at room temperature. The activation energy for alkyne rotation has been determined to be 60 ± 2 kJ mol^{-1} and the process has been modelled by extended-Hückel molecular-orbital calculations.

Heteronuclear clusters display new and interesting reactivity patterns due to co-operative effects between adjacent metal centres.[2] Metal–ligand fragments affect the electronic and steric environments of neighbouring metal sites, also transformations of organic moieties ligated to transition-metal clusters often involve multi-centre interactions.[3] Consequently, considerable effort has been directed to exploring the synthesis and reactivity of heteronuclear clusters.[4] The formation of clusters of desired metal composition and nuclearity is greatly assisted by the identification and development of rational synthetic routes.[5] One such approach is the use of ligands which promote the formation of metal–metal bonds by bridging two metal centres.[6,7] Alkynes bridge metal–metal bonds in a variety of co-ordination modes[8] and mononuclear alkyne complexes can be used as precursors to bi-and tri-metallic complexes by addition of suitable metal–ligand fragments.[9] For example, in Part 1 of this Series we reported[1] the reactions of $[W(CO)(C_2R_2)_3]$ (R = Et or Pr) with $[Co_2(CO)_8]$ which afford the trinuclear clusters $[WCo_2(\mu\text{-}C_2R_2)(\mu\text{-}C_4R_4)(CO)_8]$. We were surprised at how readily these clusters could be formed despite the fact that both π orbitals on the alkyne ligands are involved in bonding to the tungsten centre in the $[W(CO)(C_2R_2)_3]$ precursors, in which each ligand donates an average of $3\frac{1}{3}$ electrons.[10] We decided to investigate whether a complex containing a four-electron donating alkyne ligand would form clusters when treated with $[Co_2(CO)_8]$. The complexes chosen for this study were the well characterised $[W(CO)(alkyne)(S_2CNR_2)_2]$ four-electron donor alkyne systems.[11,12] A preliminary account of some of the results described herein has been given.[13]



	R	R1	R2
(1)	Et	H	H
(2)	Me	H	H
(3)	Et	Ph	Ph
(4)	Me	Ph	Ph
(5)	Me	Me	Me
(6)	Et	Ph	H

Results and Discussion

Reaction of $[Co_2(CO)_8]$ with $[W(CO)(C_2H_2)(S_2CNR_2)_2]$ (R = Et or Me) in dichloromethane at room temperature affords compounds (1) and (2) respectively (see Experimental Section). Analytical and i.r. data for the new compounds is given in Table 1. The fast-atom-bombardment mass spectrum of (2) displays isotopic envelopes corresponding to $[M - CO + H]^+$ and $[M - nCO]^+$ (n = 2—5), the base peak being $(M - 4CO)^+$. The n.m.r. spectra for (1) and (2) are analogous (see

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† 1,1,2,2-Tetracarbonyl-μ_3-[(diethylamino)thioxomethyl-*C*(Co^1)*S*-(Co^2W)]-3-diethyldithiocarbamato-3-diphenylacetylene-μ_3-sulphido-*triangulo*-dicobalt-tungsten.

Supplementary data available: see ref. 13.

Table 1. Analytical[a] and physical data for the tungsten–cobalt complexes

	Compound	Colour	Yield (%)	$\nu_{max.}$(CO)/cm^{-1}	Analysis (%) C	H	N
(1)	$[WCo_2(\mu-C_2H_2)(\mu-S)(CO)_5(SCNEt_2)(S_2CNEt_2)]$	Brown	83	2 060s, 2 015vs, 1 996m, 1 972w[b]	26.1(26.7)	2.3(2.9)	3.3(3.7)
(2)	$[WCo_2(\mu-C_2H_2)(\mu-S)(CO)_5(SCNMe_2)(S_2CNMe_2)]$	Brown	57	2 060s, 2 015vs, 1 995m, 1 973w[b]	22.1(22.0)	2.1(2.0)	3.4(4.0)
(3)	$[WCo_2(\mu-C_2Ph_2)(\mu-S)(CO)_5(SCNEt_2)(S_2CNEt_2)]$[c]	Brown	43	2 058s, 2 014s, 1 997m, 1 978w[b]			
(4)	$[WCo_2(\mu-C_2Ph_2)(\mu-S)(CO)_5(SCNMe_2)(S_2CNMe_2)]$	Brown	26	2 059s, 2 015s, 1 998m, 1 980w[b]	34.5(34.9)	2.6(2.6)	3.1(3.3)
(5)	$[WCo_2(\mu-C_2Me_2)(\mu-S)(CO)_5(SCNMe_2)(S_2CNMe_2)]$	Brown	12	2 056s, 2 009vs, 1 990m, 1 964w[b]	23.4(24.5)	2.5(2.5)	3.6(3.8)
(6)	$[WCo_2(\mu-C_2HPh)(\mu-S)(CO)_5(SCNEt_2)(S_2CNEt_2)]$[c]	Brown	55	2 056s, 2 015vs, 1 992m, 1 974w[b]			
(7)	$[WCo_2(\mu-S)(\mu-SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)]$	Purple	38	2 018s, 1 983vs, 1 956m, 1 939w(sh)[d]	37.7(37.9)	3.2(3.4)	3.1(3.2)
(8)	$[WCo_2(\mu-S)(\mu-SCNMe_2)(CO)_4(C_2Ph_2)(S_2CNMe_2)]$	Purple	29	2 019s, 1 985vs, 1 958m, 1 941w(sh)[d]	33.8(34.6)	2.5(2.7)	3.3(3.4)
(9)	$[WCo_2(\mu-S)(\mu-SCNEt_2)(CO)_4(C_2HPh)(S_2CNEt_2)]$[c]	Purple	—	2 019s, 1 984vs, 1 957m, 1 940w(sh)[d]			
(10)	$[WCo_2(\mu-S)(\mu-SCNMe_2)(CO)_4(C_2Me_2)(S_2CNMe_2)]$	Purple	22	2 015s, 1 980vs, 1 954m, 1 934w(sh)[d]	23.1(23.7)	2.4(2.6)	3.8(4.0)
(11)	$[WCo_2(\mu-S)(C_2Ph_2)(CO)_4(PPh_3)(SCNEt_2)(S_2CNEt_2)]$	Brown	90	2 010m, 1 982vs, 1 961m[d]	47.7(48.0)	4.0(3.9)	2.2(2.4)
(12)	$[WCo_2(\mu-S)(C_2H_2)(CO)_4(PPh_3)(SCNMe_2)(S_2CNMe_2)]$	Brown	89	2 013m, 1 984vs, 1 962m[d]	38.7(38.2)	3.2(3.1)	3.0(3.0)

[a] Calculated values are given in parentheses. [b] In light petroleum. [c] Incomplete data (see text). [d] In CH_2Cl_2.

Table 2) and only the spectra of (**1**) will be discussed in detail. The ^{1}H n.m.r. spectrum of (**1**) contains signals due to four non-equivalent ethyl groups and two signals at δ 8.27 and 6.62 assigned to the two ethyne protons. In the precursor, $[W(CO)(C_2H_2)(S_2CNEt_2)_2]$, both these protons are equivalent at room temperature and have a chemical shift of δ 13.05, characteristic of ethyne acting as a terminally bound, four-electron donor ligand.[12] The change in the ^{1}H n.m.r. characteristics of this ligand indicate a significant change in bonding mode and, most probably, the ethyne in (**1**) is bridging a metal–metal bond.[1] The ^{13}C n.m.r. spectrum provides further information concerning the ligation of the ethyne. Resonances at δ 112.4 [^{1}J(CH) 217, ^{2}J(CH)7 Hz] and 108.3 p.p.m. [^{1}J(CH)209, [^{2}J(CH)8 Hz] are assigned to acetylenic carbons, and the ^{1}H-decoupled spectrum reveals tungsten satellite peaks about both resonances, ^{1}J(WC) = 16 and 28 Hz, respectively. Again the chemical shifts indicate that the ethyne is no longer a terminally bound four-electron donor and is likely to be a bridging ligand in view of its static nature.[1] The tungsten satellites indicate that it is bridging a W–Co bond. The ^{13}C-{^{1}H} n.m.r. spectrum of compound (**1**) also contains four methyl resonances, but only three resolved methylene resonances at δ 52.3, 45.1, and 44.3 p.p.m. The last two resonances are typical of a diethyldithiocarbamato ligand, while the first is characteristic of a diethylthiocarboxamido ligand. For example, the spectrum of $[W(CO)(C_2H_2)(S_2CNEt_2)_2]$ contains methylene resonances at δ 44.2, 44.5, and 46.0 p.p.m.,[12] while $[W(S)(C_2Ph_2)(S_2CNEt_2)(SCNEt_2)]$ displays resonances at δ 45.2, 50.3, and 54.4 p.p.m.[14] All four of the expected methyl resonances are observed in the ^{13}C-{^{1}H} n.m.r. spectrum of (**2**), but they are divided into two groups, δ 39.0, 39.8 and 49.1, 47.2 p.p.m. Transformation of dithiocarbamate ligands into thiocarboxamide ligands at tungsten centres is well established[15,16] and is confirmed by inspection of the low-field region of the spectrum. For compound (**1**), the dithiocarbamate resonance occurs at δ 206.5 p.p.m. while the thiocarboxamide carbon resonance occurs at δ 247.2 p.p.m. and can be compared with those for $[W(S)(C_2Ph_2)(S_2CNEt_2)(SCNEt_2)]$ (δ 257.5 p.p.m.)[14] and $[W(CO)(PhCHS)(S_2CNEt_2)(SCNEt_2)]$[δ 256.9 p.p.m. J(WC) 111 Hz].[16] Tungsten satellites about this sharp resonance [J(WC) 79 Hz] indicate that this carbon is directly attached to tungsten. The remaining peaks in the spectrum are two broad resonances due to carbonyls on cobalt, there being no tungsten carbonyl resonance. The proposed structure is based on the n.m.r. evidence presented above and on comparison with the spectroscopic characteristics of (**7**) whose structure has been determined by an *X*-ray diffraction study (see below).

Compounds (**3**)—(**6**), analogous to (**1**) and (**2**), can be prepared *via* the reactions of $[W(CO)(R^1C_2R^2)(S_2CNR_2)_2]$ (R^1 = H, R^2 = Ph; R^1 = R^2 = Me or Ph with $[Co_2(CO)_8]$. In general the dimethyldithiocarbamate derivatives are less soluble in organic solvents than the diethyldithiocarbamate derivatives. Compound (**4**) was insufficiently soluble to allow the recording of reasonable quality n.m.r. spectra, while instability in solution precluded the unambiguous assignment of all the resonances in the ^{13}C-{^{1}H} spectrum of (**6**) and the relative positions of the hydrogen and phenyl substituents have not been determined.

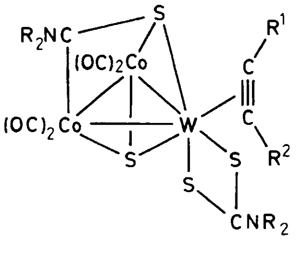
Although (**1**) and (**2**) are stable in solution at room temperature, all the other derivatives of this type are unstable with respect to carbonyl loss and rearrangement to compounds (**7**)—(**10**) over a period of several hours in solution. A crystal structure of (**7**) established the formulation of these compounds and will be described before their spectroscopic characteristics.

Selected structural parameters for compound (**7**) are listed in Table 3 and the molecular structure is shown in Figure 1. The cluster has a triangular core of metal atoms [W–Co(1) 2.701(1), W–Co(2) 2.601(1), Co(1)–Co(2) 2.492(1) Å] capped on one side by a μ_3-sulphido ligand and on the other by a μ_3-diethylthiocarboxamido moiety bound through the carbon to Co(1) [1.900(6) Å] and through the sulphur to Co(2) [2.239(2) Å] and to W [2.450(1) Å]. This represents a considerable rearrangement from (**3**) in which the thiocarboxamido was bound through the carbon to tungsten. Thiocarboxamido ligands have been previously observed to bond simultaneously to two metal

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the tungsten–cobalt complexes

Compound	^{1}H(δ)[b]	^{13}C(δ)[c]
(1)	8.27 (s, 1 H, CH), 6.62 (s, 1 H, CH), 4.1—3.4 (m, 8 H, CH$_2$), 1.40 [t, 3 H, Me, *J*(HH) 7], 1.28 [t, 3 H, Me, *J*(HH) 7], 1.25 [t, 3 H, Me, *J*(HH) 7], 1.05 [t, 3 H, Me, *J*(HH) 7]	247.2 [S*C*NEt$_2$, *J*(WC) 79], 211.5 (CO), 206.5 (S$_2$*C*NEt$_2$), 199.0 (CO), 112.4 [CH, *J*(WC) 16], 108.3 [CH, *J*(WC) 28], 52.3 [SCN(*C*H$_2$Me)$_2$], 45.1 44.3 [S$_2$CN(*C*H$_2$Me)$_2$], 15.5, 12.8, 12.7, 12.2 (Me)
(2)	8.30 (s, 1 H, CH), 6.82 (s, 1 H, CH), 3.70 (s, 3 H, Me), 3.60 (s, 3 H, Me), 3.30 (s, 3 H, Me), 3.16 (s, 3 H, Me)	249.2 (S*C*NMe$_2$), 211.2 (CO), 207.8 (S$_2$*C*NMe$_2$), 198.7 (CO), 113.3 (CH), 107.9 [CH, *J*(WC) 29], 49.1, 47.2 (SCN*Me*$_2$), 39.8, 39.0 (S$_2$CN*Me*$_2$)
(3)	[d]7.9 – 6.6 (m, 10 H, Ph), 4.4—3.2 (m, 8 H, CH$_2$), 1.6—1.0 (m, 12 H, Me)	244.7 [S*C*NEt$_2$, *J*(WC) 81], 212.7 (CO), 211.2 (CO), 205.7 (S$_2$*C*NEt$_2$), 199.4 (CO), 141.8, 139.8 (2 × *ipso*-C), 135.8 (*C*Ph), 132.7—127.3 (Ph), 123.7 (*C*Ph), 52.6—44.1 (CH$_2$), 15.7—11.8 (Me)
(5)	3.64 (s, 3 H, Me), 3.53 (s, 3 H, Me), 3.25 (s, 3 H, Me), 3.12 (s, 3 H, Me), 2.90 (s, 3 H, C$_2$Me$_2$), 2.39 (s, 3 H, C$_2$Me$_2$)	249.9 (S*C*NMe$_2$), 206.2 (S$_2$*C*NMe$_2$), 132.2, 127.7 (*C*$_2$Me$_2$), 47.7, 45.8 (SCN*Me*$_2$), 38.5, 37.9 (S$_2$CN*Me*$_2$), 16.3, 14.3 (C$_2$*Me*$_2$)
(6)	8.62 (s, 1 H, CH), 7.4—6.6 (m, 5 H, Ph), 4.2—3.2 (m, 8 H, CH$_2$), 1.6—0.7 (m, 12 H, Me)	[e]245.9 (S*C*NEt$_2$), 210.8 (CO), 204.8 (S$_2$*C*NEt$_2$), 198.4 (CO), 120.1 (CPh), 113.6 (CH)
(7)	[d]8.40—7.20 (m, 10 H, Ph), 4.28—4.00 (m, 4 H, CH$_2$), 3.73—3.62 (m, 1 H, CH$_2$), 3.48—3.29 (m, 3 H, CH$_2$), 1.47 [t, 3 H, Me, *J*(HH) 7], 1.33 [t, 3 H, Me, *J*(HH) 7], 1.09 [t, 3 H, Me, *J*(HH) 7], 1.08 [t, 3 H, Me, *J*(HH) 7]	[f]227.5 (S*C*NEt$_2$), 202.0 (*C*Ph), 201.1 (S$_2$*C*NEt$_2$), 199.9 (*C*Ph), 197.5, 194.8 (CO), 138.2, 135.8 (2 × *ipso*-C), 130.7, 129.9 (2 × *m*-C), 129.2, 129.0 (2 × *p*-C), 128.1, 127.8 (2 × *o*-C), 51.2, 49.3 [SCN(*C*H$_2$Me)$_2$], 44.4, 44.3 [S$_2$CN(*C*H$_2$Me)$_2$], 12.7, 12.0, 11.5, 11.1 (Me)
(8)	8.30—7.40 (m, 10 H, Ph), 3.80 (s, 3 H, Me), 3.61 (s, 3 H, Me), 3.10 (s, 3 H, Me), 3.04 (s, 3 H, Me)	[e]131.4, 130.2, 129.1 (Ph), 47.1, 46.2 (SCN*Me*$_2$), 40.1 (S$_2$CN*Me*$_2$)
(9)	11.93 (s, 1 H, CH), 8.1—6.7 (m, 5 H, Ph), 4.3—3.3 (m, 8 H, CH$_2$), 1.6—1.0 (m, 12 H, Me)	[e]229.5 (S*C*NEt$_2$), 201.7 (S$_2$*C*NEt$_2$), 193.4 (*C*Ph), 189.3 (CH), 132.0, 129.2, 128.0 (Ph), 51.4, 49.3 [SCN(*C*H$_2$Me)$_2$], 44.5, 44.3 [S$_2$CN(*C*H$_2$Me)$_2$], 12.6, 12.0, 11.5, 11.1 (Me)
(10)	3.72 (s, 3 H, Me), 3.56 (s, 3 H, Me), 3.22 (s, 3 H, Me), 3.04 (s, 3 H, Me), 2.90 (s, 6 H, C$_2$Me$_2$)	231.5 (S*C*NMe$_2$), 207.4 (S$_2$*C*NMe$_2$), 203.6 (CO), 200.7 (CO), 199.1 [*C*$_2$Me$_2$, *J*(WC) 39], 47.2, 45.9 (SCN*Me*$_2$), 40.1, 40.0 (S$_2$CN*Me*$_2$), 20.7 (C$_2$*Me*$_2$)
(12)	[d]7.92 (s, 1 H, CH), 7.7—7.2 (m, 15 H, Ph), 6.21 (s, 1 H, CH), 3.60 (s, 6 H, 2 × Me), 3.18 (s, 3 H, Me), 3.12 (s, 3 H, Me)	[e]249.5 (S*C*NMe$_2$), 207.5 (S$_2$*C*NMe$_2$), 136—127 (Ph), 108.1, 105.1 (C$_2$H$_2$), 47.5, 45.7 (SCN*Me*$_2$), 38.5, 37.8 (S$_2$CN*Me*$_2$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD$_2$Cl$_2$ unless otherwise stated. [c] Measured in CD$_2$Cl$_2$, hydrogen-1 decoupled, measurements at room temperature unless otherwise stated. [d] Measured in CDCl$_3$. [e] Incomplete data (see text). [f] Measured at 233 K.



	R	R^1	R^2
(7)	Et	Ph	Ph
(8)	Me	Ph	Ph
(9)	Et	Ph	H
(10)	Me	Me	Me

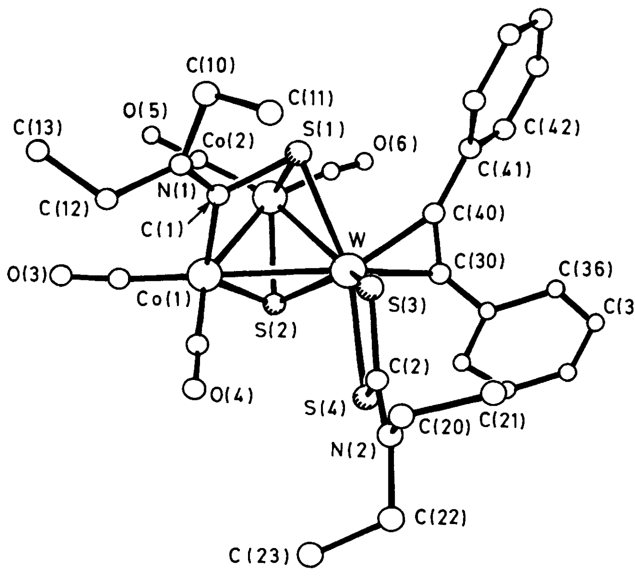


Figure 1. The molecular structure of [WCo$_2$(μ-S)(μ-SCNEt$_2$)(CO)$_4$(C$_2$Ph$_2$)(S$_2$CNEt$_2$)] (7) showing the atom-labelling scheme

centres,[17–19] but we believe that this is the first example of a thiocarboxamido ligand adopting a μ$_3$-bonding mode. The distance Co(1)–C(1) [1.900(6) Å] is shorter than the corresponding distance in [Co$_3$(μ$_3$-S)(μ-SCNMe$_2$)(CO)$_7$] [1.958(5) Å], and is in the range for transition-metal-stabilised carbenes.[18] However, the C(1)-N(1) bond [1.314(8) Å] also has a high degree of double-bond character and is comparable with C(2)-N(2) [1.308(8) Å]. The C(1)-S(1) distance [1.772(6) Å] indicates little multiple bond character and is significantly longer than the corresponding length in other ligated thiocarboxamido ligands.[15,17–19] This weakening of the C-S bond can be ascribed

Table 3. Selected internuclear distances (Å) and angles (°) for [$WCo_2(\mu$-$S)(\mu$-$SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)$] (**7**), with estimated standard deviations (e.s.d.s) in parentheses

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(1)–C(3)	1.787(8)
Co(1)–C(4)	1.746(7)	Co(2)–S(1)	2.239(2)
Co(2)–S(2)	2.190(2)	Co(2)–C(5)	1.770(7)
Co(2)–C(6)	1.805(7)	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)	N(1)–C(10)	1.490(9)
N(1)–C(12)	1.468(9)	C(2)–N(2)	1.308(8)
N(2)–C(20)	1.479(9)	N(2)–C(22)	1.479(8)
C(3)–O(3)	1.137(10)	C(4)–O(4)	1.156(9)
C(5)–O(5)	1.137(9)	C(6)–O(6)	1.116(9)
C(30)–C(31)	1.476(8)	C(30)–C(40)	1.316(8)
C(40)–C(41)	1.459(7)		

W–Co(1)–Co(2)	60.0(1)	W–Co(2)–Co(1)	64.0(1)
Co(1)–W–Co(2)	56.0(1)	S(3)–W–S(4)	70.7(1)
W–S(1)–Co(2)	67.2(1)	W–S(1)–C(1)	88.8(2)
Co(2)–S(1)–C(1)	87.6(2)	W–S(2)–Co(1)	72.7(1)
W–S(2)–Co(2)	69.9(1)	Co(1)–S(2)–Co(2)	69.0(1)
Co(1)–C(3)–O(3)	175.5(9)	Co(1)–C(4)–O(4)	176.7(7)
Co(2)–C(5)–O(5)	177.9(7)	Co(2)–C(6)–O(6)	172.6(7)
Co(1)–C(1)–S(1)	106.5(3)	Co(1)–C(1)–N(1)	135.4(4)
S(1)–C(1)–N(1)	118.0(4)	C(30)–C(40)–C(41)	142.2(5)
C(31)–C(30)–C(40)	138.1(5)	C(30)–W–C(40)	37.7(2)

to the simultaneous co-ordination to three metal centres in which the ligand acts as a five-electron donor.

The two cobalt centres are also ligated by two terminal carbonyl ligands while the tungsten atom is ligated by a chelating diethyldithiocarbamate group and, surprisingly, a terminally bound diphenylacetylene. The alkyne carbon–carbon bond length is 1.316(8) Å and the phenyl substituents are bent back by angles of 41.9(5) [C(31)] and 37.8(5)° [C(41)] from linear. These parameters are relatively insensitive to whether the alkyne is formally a two-or four-electron donor. However, the tungsten–carbon bond distances [W–C(30) 2.034(5), W–C(40) 2.044(5) Å] are indicative of a four-electron interaction and can be compared with those found in [$W(CO)(C_2H_2)(S_2CNEt_2)_2$] (2.03 ± 0.01 Å).[11] This leads to a formal cluster valence-electron count of 48 as expected for a triangular cluster.

The bonding parameters determined by the single-crystal *X*-ray diffraction study of compound (**7**) are reflected in its solution n.m.r. properties. The ^{13}C-{^{1}H} n.m.r. spectrum recorded at 233 K contains two peaks assigned to the alkyne carbons at δ 202.0 and 199.9 p.p.m. in the region expected for a four-electron donor alkyne.[20] The thiocarboxamido carbon attached to cobalt occurs at δ 227.5 p.p.m. and the methylene carbons are at δ51.2 and 49.3 p.p.m., downfield of the methylene carbons of the dithiocarbamate (δ 44.4 and 44.3 p.p.m.). Warming the sample to 338 K leads to coalescence of the signals due to the diphenylacetylene, indicating rotation of the alkyne about a vector between the tungsten and the centre of the carbon–carbon bond.[12] No coalescence is observed for the resonances due to the ethyl groups of the dithiocarbamato and thiocarboxamido ligands, reflecting the multiple bond character of the C–N linkages. The rotational activation barrier for the alkyne, $\Delta G^{\neq}$, was calculated from the Eyring equation, after the Gutowsky–Holm equation was employed to calculate k_{ex} at the coalescence temperature,[21] and found to be 60 ± 2 kJ mol^{-1}. This is higher than the value of 49 ± 0.5 kJ mol^{-1} determined for [$W(CO)(C_2H_2)(S_2CNEt_2)_2$].[12]

The role of ligand π donation in formally electron-deficient organometallic Group 6 complexes has been explored by Templeton *et al.*[22] using extended–Hückel molecular orbital theory. It was shown that electronic factors are important in determining the conformations of a number of metal alkyne complexes. In order to establish whether the same was true for (**7**), similar calculations were performed on the model compound [$WCo_2(\mu$-$S)(\mu$-$SCNH_2)(CO)_4(C_2H_2)(S_2CNH_2)$]. Details of the calculations and the molecular geometry are given in the Experimental Section. The alkyne was rotated by angles θ about a vector between the tungsten and the centre of the carbon–carbon bond and total energies were sampled at 15° intervals between −100 and +120°. The results are illustrated in Figure 2 and show a potential well of approximately 62 kJ mol^{-1}, which is remarkably close to the experimental result for compound (**7**). As can be seen from Figure 2 the minimum-energy orientation for the model compound corresponds to only a 15° rotation from the crystallographically determined orientation of the alkyne in compound (**7**).

The n.m.r. spectra of compounds (**8**)—(**10**) (Table 2) show that they are analogous to (**7**). Low solubility of (**8**) precluded the acquisition of a ^{13}C-{^{1}H} spectrum of sufficient quality to allow a full assignment, while observation of the broad carbonyl resonances in the spectrum of (**9**) was hampered by the instability of the compound. The ^{1}H n.m.r. spectrum of (**9**) contains a resonance assigned to the acetylenic proton at δ 11.93, at a similar chemical shift to that found for [$W(CO)(HC_2Ph)(S_2CNEt_2)_2$] (δ 13.34),[12] and markedly shifted from its position of δ 8.62 in the spectrum of (**6**).

As mentioned earlier, (**1**) and (**2**) are stable with respect to carbonyl loss and rearrangement to compounds analogous to (**7**). Compound (**2**) does however undergo carbonyl substitution with PPh_3 to afford (**12**), and, in a similar manner, (**3**) reacts with PPh_3 to afford (**11**). Both compounds are unstable with respect to phosphine loss in solution unless there is an excess of phosphine present. Decomposition leads to the formation of the precursors (**2**) and (**3**) as the only identifiable products. The n.m.r. data for of (**12**) are in Table 2 and are similar to those for (**2**) with the addition of resonances due to the PPh_3 group.

Experimental

The experimental techniques used and the instrumentation employed have been described previously.[1] The compounds [$W(CO)(alkyne)(S_2CNR_2)_2$] were prepared by literature methods.[12] Analytical and other data for the new compounds are given in Tables 1 and 2.

Preparations.—[$WCo_2(\mu$-$C_2H_2)(\mu$-$S)(CO)_5(SCNR_2)(S_2CNR_2)$] [R = Et (**1**) *or* Me (**2**)]. A solution of [$W(CO)(C_2H_2)(S_2CNEt_2)_2$] (0.47 g, 0.88 mmol) and [$Co_2(CO)_8$] (0.33 g, 0.96 mmol) in CH_2Cl_2 (15 cm^3) was stirred for 1 h after which time it was filtered through an alumina pad (1.5 × 3 cm). Reduction of the solvent *in vacuo* to *ca.* 2 cm^3, followed by addition of light petroleum (b.p. 40—60 °C) afforded microcrystals of compound (**1**) (0.56 g, 0.63 mmol). Compound (**2**) was prepared in an analogous manner.

[$WCo_2(\mu$-$R^1C_2R^2)(\mu$-$S)(CO)_5(SCNR_2)(S_2CNR_2)$][$R^1$ = R^2 = Ph, R = Et (**3**) *or* Me (**4**); R^1 = R^2 = R = Me (**5**); R^1 = Ph, R^2 = H, R = Et (**6**)] *and* [$WCo_2(\mu$-$S)(\mu$-$SCNR_2)(CO)_4(R^1C_2R^2)(S_2CNR_2)$] [$R^1$ = R^2 = Ph, R = Et (**7**) *or* Me (**8**); R^1 = Ph, R^2 = H, R = Et (**9**); R^1 = R^2 = R = Me (**10**)]. A solution of [$W(CO)(C_2Ph_2)(S_2CNEt_2)_2$] (0.65 g, 0.95 mmol) and [$Co_2(CO)_8$] (0.46 g, 1.35 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 24 h after which time it was filtered through an

Table 4. Atomic co-ordinates (× 10^4), with e.s.d.s. in parentheses, for complex (7)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 242(1)	6 446(1)	6 653(1)	C(4)	−1 409(7)	6 911(4)	5 444(4)
Co(1)	44(1)	7 382(1)	5 547(1)	O(4)	−2 385(5)	6 622(3)	5 401(4)
Co(2)	2 363(1)	7 549(1)	6 125(1)	C(5)	2 449(8)	8 399(4)	5 631(4)
S(1)	1 453(2)	7 766(1)	7 077(1)	O(5)	2 521(7)	8 956(3)	5 334(3)
S(2)	1 552(2)	6 571(1)	5 443(1)	C(6)	4 023(7)	7 304(4)	6 468(4)
S(3)	−510(2)	6 324(1)	7 282(1)	O(6)	5 037(5)	7 112(3)	6 611(4)
S(4)	−84(1)	5 309(1)	6 148(1)	C(30)	2 676(5)	5 711(3)	7 093(3)
C(1)	25(6)	7 978(3)	6 403(3)	C(31)	3 338(5)	4 985(3)	7 061(3)
N(1)	−781(5)	8 452(3)	6 591(3)	C(32)	3 239(6)	4 615(4)	6 388(4)
C(10)	−607(7)	8 807(4)	7 343(4)	C(33)	3 914(7)	3 948(4)	6 375(4)
C(11)	−1 049(8)	8 309(4)	7 888(4)	C(34)	4 637(7)	3 638(4)	7 008(5)
C(12)	−1 964(8)	8 671(4)	6 054(4)	C(35)	4 718(7)	4 003(4)	7 679(4)
C(13)	−1 877(11)	9 448(5)	5 729(6)	C(36)	4 077(6)	4 669(3)	7 717(4)
C(2)	−1 026(5)	5 517(3)	6 750(3)	C(40)	2 781(5)	6 303(3)	7 537(3)
N(2)	−2 040(4)	5 137(3)	6 804(3)	C(41)	3 596(5)	6 631(3)	8 212(3)
C(20)	−2 804(6)	5 360(4)	7 337(4)	C(42)	4 922(6)	6 512(4)	8 389(4)
C(21)	−2 284(8)	5 036(4)	8 102(4)	C(43)	5 678(7)	6 828(4)	9 032(4)
C(22)	−2 501(6)	4 476(4)	6 320(4)	C(44)	5 139(8)	7 237(4)	9 508(4)
C(23)	−3 499(7)	4 705(5)	5 634(4)	C(45)	3 852(7)	7 351(4)	9 348(4)
C(3)	−251(9)	7 960(5)	4 727(4)	C(46)	3 077(6)	7 044(4)	8 706(3)
O(3)	−509(9)	8 344(4)	4 217(4)				

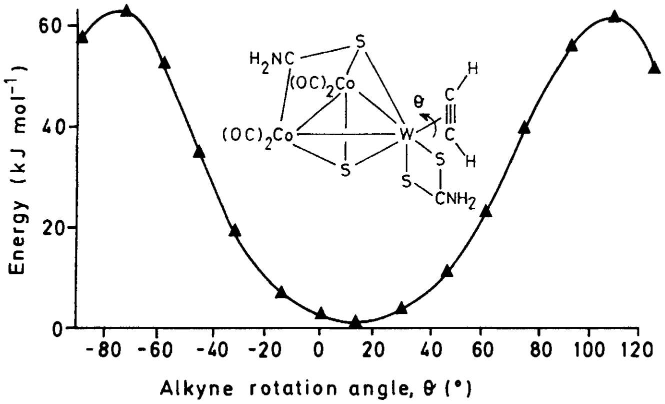
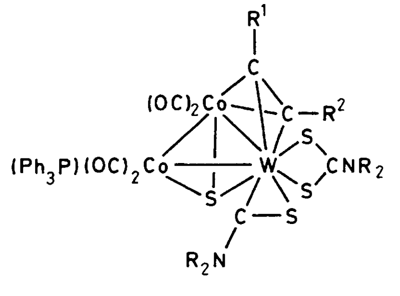


Figure 2. Relative calculated total energy *vs.* the alkyne rotation angle for [$WCo_2(\mu$-$S)(\mu$-$SCNH_2)(CO)_4(C_2H_2)(S_2CNH_2)$]



	R	R^1	R^2
(11)	Et	Ph	Ph
(12)	Me	H	H

alumina pad (1.5 × 3 cm). The solvent was removed *in vacuo* and the residue chromatographed on an alumina column (1.5 × 15 cm), eluting with CH_2Cl_2–light petroleum (1:3). Two major bands, brown (**3**) (0.37 g, 0.40 mmol) followed by purple (**7**) (0.32 g, 0.36 mmol), were eluted. The related compounds (**6**), (**9**) and (**5**), (**10**) were prepared in a similar manner.

[$WCo_2(\mu$-$R^1C_2R^2)(\mu$-$S)(CO)_4(PPh_3)(SCNR_2)(S_2CNR_2)$] [$R^1 = R^2 =$ Ph, R = Et (**11**); $R^1 = R^2 =$ H, R = Me (**12**)].—A solution of compound (**3**) (0.37 g, 0.40 mmol) and PPh_3 (0.11 g, 0.40 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 3 h. Filtration of the solution through an alumina pad (1.5 × 5 cm) followed by removal of the solvent *in vacuo* afforded (**11**) (0.42 g, 0.36 mmol). Compound (**12**) was prepared in a similar manner by the reaction of (**2**) with PPh_3.

Calculations.—The calculational method employed was the extended-Hückel approach described by Hoffmann.[23] The program FORTICON 8 (QCPE 344) as available at the University of London Computer Centre on the Amdahl computer was used for the calculations. Parameters for cobalt and tungsten were taken from ref. 24. The crystallographic co-ordinates of compound (**7**) were used to generate the geometry of the model compound [$WCo_2(\mu$-$S)(\mu$-$SCNH_2)(CO)_4(C_2H_2)(S_2CNH_2)$] with the N-H and C-H distances set at 1.02 and 1.07 Å respectively.

Crystal Structure Determination of [$WCo_2(\mu$-$S)(\mu$-$SCNEt_2)(CO)_4(C_2Ph_2)(S_2CNEt_2)$] (**7**).—Crystals of compound (**7**) were grown from CH_2Cl_2–light petroleum. Diffracted intensities were collected at 293 K from a crystal of dimensions *ca.* 0.65 × 0.30 × 0.25 mm using a Nicolet *P*3*m* diffractometer. Of the 6 783 data (Wyckoff ω scans, $4 \leqslant 2\theta \leqslant 50°$), 4 611 unique data had $I \geqslant 2.5\sigma(I)$ and only these were used in structure solution and refinement, after the data had been corrected for Lorentz, polarisation and *X*-ray absorption effects, the last by an empirical method based on azimuthal scan data.[25]

Crystal data. $C_{28}H_{30}Co_2N_2O_4S_4W$, $M = 888.5$, monoclinic, $a = 10.798(4)$, $b = 17.658(4)$, $c = 18.421(6)$ Å, $\beta = 103.88(3)°$, $U = 3\,410(2)$ Å^3, $Z = 4$, $D_c = 1.73$ g cm^{-3}, $F(000) = 1\,744$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 46.7 cm^{-1}.

The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and Fourier difference methods. Hydrogen atoms were included in calculated positions with either fixed isotropic thermal parameters *ca.* $1.2U_{iso}$ of the parent carbon atoms (phenyl and methylene) or common refined isotropic thermal parameters (methyl). All non-hydrogen atoms had anisotropic thermal parameters. Refinement by blocked-cascade least squares led to $R = 0.031$ ($R' = 0.032$)

with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.0005|F^2|]$. The final electron-density difference synthesis showed no peaks $\geqslant 0.5$ or $\leqslant -0.5$ e Å^{-3}. Scattering factors and corrections for anomalous dispersion were from ref. 26. All computations were carried out on an Eclipse Data General computer with the SHELXTL system of programs.[25] Atomic positional parameters are given in Table 4.

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