Reactions of the Complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with Dithiocarbamates and Related Ligands, and the *X*-Ray Crystal Structure of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$†

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The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) react with 1 equivalent of S_2CX^- [X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}] in CH_2Cl_2 or Et_2O at room temperature eventually to give the new bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$. Infrared spectral studies of the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equivalent of $Na[S_2CNEt_2]\cdot 3H_2O$ in CH_2Cl_2 suggest the formation of several intermediates including those with monodentate dithiocarbamate attached to tungsten. *X*-Ray single-crystal studies were carried out on the compound $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ (**9**). Crystals of (**9**) are monoclinic, space group $P2_1/n$, in a unit cell of dimensions a = 9.256(8), b = 17.685(14), c = 10.962(11) Å, and β = 90.5(1)°. The structure was refined to R = 0.061 for 2 097 reflections above background. The co-ordination geometry around the tungsten is octahedral with the two parallel *cis*-but-2-yne ligands *trans* to a sulphur and an iodide with the other sulphur of the dithiocarbamate and the carbonyl ligand occupying the axial sites. Variable-temperature ^1H n.m.r. studies show complex (**9**) to be fluxional in solution. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ also react with 2 equivalents of S_2CX^- [R = Me, X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}; R = Ph, X = NEt_2 or OEt] to give the monoalkyne complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$. ^{13}C N.m.r. spectroscopy shows that the alkyne ligands in the bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ are donating an average of three electrons each to the metal, whereas the alkyne ligand in $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ is donating four electrons to the tungsten.

Alkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention in recent years.[1–6] A variety of such complexes containing two dithiocarbamates or related ligands have been reported. For example, the complexes $[Mo(CO)_2(S_2CNEt_2)_2]$ react with RC_2R' (R = R' = H, Ph, or CO_2Me; R = H, R' = Me or Ph; R = Me, R' = Ph) to give $[Mo(CO)(S_2CNEt_2)_2(\eta^2\text{-}RC_2R')]$.[7] Complexes of this type can also be prepared by treating $[Mo(CO)_2L(S_2CNEt_2)_2]$ (L = CO or PPh_3) or $[Mo(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ with an alkyne to give the L or HC_2H substituted products.[8] In 1975 the dithiophosphinate complex $[Mo(CO)(S_2PPr^i{}_2)_2(\eta^2\text{-}HC_2H)]$ was reported.[9,10] Tungsten analogues of the bis(dithiocarbamate) complexes $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}RC_2R')]$ (R = R' = H, Me, Et, or Ph; R = H, R' = Ph) have been prepared by treating $[W(CO)_2L(S_2CNEt_2)_2]$ (L = CO[11] and PPh_3[12]) with 1 equivalent of RC_2R'. Bennett and Boyd[13] reported the preparation of the cyclo-octyne complexes $[M(CO)(S_2CNR_2)_2(\eta^2\text{-}C_8H_{12})]$ (M = Mo or W, R = Me or Et) by this method. Very recently Carlton and Davidson[14] described the reactions of the bromo-bridged dimers, $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2\}_2]$ with NaS_2PMe_2, NaS_2CNMe_2, or $Tl(2\text{-}SC_5H_4N)$ to give the monoalkyne complexes $[W(CO)(L\text{–}L')_2(\eta^2\text{-}RC_2R')]$ (R = R' = Me, L–L' = S_2CNMe_2 or 2-SC_5H_4N; R = Ph, R' = Me, L–L' = S_2CNMe_2 or S_2PMe_2; R = R' = Ph, L–L' = S_2PMe_2) or the bis(alkyne) compound $[W(2\text{-}SC_5H_4N)_2(\eta^2\text{-}PhC_2Ph)_2]$. Apart from the recent work of Davidson and Vasapollo[15] describing the preparation of $[WBr(CO)(L\text{–}L)(\eta^2\text{-}MeC_2Me)_2]$ [L–L = S_2CNMe_2, S_2PMe_2, or acetylacetonate (acac)] no other examples of monodithiocarbamate type bis(alkyne) complexes of molybdenum(II) or tungsten(II) have been reported.

In recent years we have been investigating the chemistry of the highly versatile complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph)[16] prepared in quantitative yield from reaction of $[WI_2(CO)_3(NCMe)_2]$ with 2 equivalents of RC_2R. In this paper we describe the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with dithiocarbamates and related ligands. The first *X*-ray crystal structure of a monodithiocarbamate bis(alkyne) complex, namely $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$, is also described.

Results and Discussion

Equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) and S_2CX^- [X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}] react in CH_2Cl_2 or Et_2O at room temperature eventually to give good yields of the new bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ (**1**)—(**12**), whereas reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with 2 equivalents of S_2CX^- [R = Me, X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}; R = Ph, X = NEt_2 or OEt] in CH_2Cl_2 at room temperature affords the monoalkyne complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ (**13**)—(**20**). All complexes (**1**)—(**20**) were fully characterised by elemental analysis (C, H, and N) and i.r. (Table 1), ^1H and, in selected cases, ^{13}C n.m.r. spectroscopy (Tables 2 and 3). The complexes (**5**), (**12**), (**16**), (**17**), and

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† Bis(η^2-but-2-yne)carbonyliodo(pyrrolidine-1-carbodithioato)tungsten(II).

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Table 1. Physical, analytical,[a] and i.r. data for the complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ and $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$

	Complex	Colour	Yield/%	Analysis/%			I.r. (cm^{-1})[b]	
				C	H	N	ν(CO)	ν(C≡C)
(1)	$[WI(CO)(S_2CNMe_2)(\eta^2\text{-}MeC_2Me)_2]$	Golden	61	24.8 (25.4)	3.2 (3.2)	2.5 (2.5)	2 040s	—
(2)	$[WI(CO)(S_2CNMe_2)(\eta^2\text{-}PhC_2Ph)_2]$	Golden	47	46.7 (47.1)	3.1 (3.2)	1.5 (1.7)	2 070s	—
(3)	$[WI(CO)(S_2CNEt_2)(\eta^2\text{-}MeC_2Me)_2]$	Golden	63	28.1 (28.3)	4.2 (3.7)	1.9 (2.4)	2 048s	—
(4)	$[WI(CO)(S_2CNEt_2)(\eta^2\text{-}PhC_2Ph)_2]$	Golden	57	48.6 (48.4)	3.7 (3.6)	1.2 (1.7)	2 075s	—
(5)	$[WI(CO)\{S_2CN(CH_2Ph)_2\}(\eta^2\text{-}MeC_2Me)_2]\cdot 0.5CH_2Cl_2$	Golden	53	37.8 (37.3)	3.6 (3.5)	1.8 (1.7)	2 048s	—
(6)	$[WI(CO)\{S_2CN(CH_2Ph)_2\}(\eta^2\text{-}PhC_2Ph)_2]$	Golden	54	53.9 (54.6)	3.6 (3.5)	1.7 (1.5)	2 075s	—
(7)	$[WI(CO)(S_2COEt)(\eta^2\text{-}MeC_2Me)_2]$	Yellow	56	24.8 (25.4)	2.9 (3.0)	— —	2 046s	—
(8)	$[WI(CO)(S_2COEt)(\eta^2\text{-}PhC_2Ph)_2]$	Golden	46	46.9 (47.1)	3.3 (3.1)	— —	2 080s	—
(9)	$[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$	Golden	90	28.9 (28.4)	3.3 (3.4)	2.7 (2.4)	2 045s	—
(10)	$[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}PhC_2Ph)_2]$	Golden	62	48.6 (48.5)	3.6 (3.4)	1.6 (1.7)	2 075s	—
(11)	$[WI(CO)(S_2CNC_5H_{10})(\eta^2\text{-}MeC_2Me)_2]$	Golden	73	30.6 (29.7)	4.0 (3.7)	2.7 (2.3)	2 042s	—
(12)	$[WI(CO)(S_2CNC_5H_{10})(\eta^2\text{-}PhC_2Ph)_2]\cdot CH_2Cl_2$	Golden	46	45.0 (46.0)	3.9 (3.4)	1.0 (1.5)	2 080s	—
(13)	$[W(CO)(S_2CNMe_2)_2(\eta^2\text{-}MeC_2Me)]$	Green	70	25.6 (26.1)	3.7 (3.6)	5.2 (5.5)	1 900s	1 650vw
(14)	$[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$	Green	73	31.9 (32.0)	4.8 (4.7)	4.7 (5.0)	1 895s	1 690vw
(15)	$[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}PhC_2Ph)]$	Green	46	42.9 (43.7)	4.5 (4.4)	4.1 (4.1)	1 915s	1 670vw
(16)	$[W(CO)\{S_2CN(CH_2Ph)_2\}_2(\eta^2\text{-}MeC_2Me)]\cdot 0.5CH_2Cl_2$	Green	47	50.5 (50.0)	4.2 (4.1)	3.5 (3.3)	1 905s	1 680vw
(17)	$[W(CO)(S_2COEt)_2(\eta^2\text{-}MeC_2Me)]\cdot Et_2O$	Brown	53	30.6 (30.9)	4.7 (4.5)	— —	1 922s	1 632vw
(18)	$[W(CO)(S_2COEt)_2(\eta^2\text{-}PhC_2Ph)]$	Green	54	39.6 (39.9)	3.0 (3.2)	— —	1 943s	1 650vw
(19)	$[W(CO)(S_2CNC_4H_8)_2(\eta^2\text{-}MeC_2Me)]$	Dark green	73	31.8 (32.3)	4.0 (4.0)	5.1 (5.0)	1 890s	1 620vw
(20)	$[W(CO)(S_2CNC_5H_{10})_2(\eta^2\text{-}MeC_2Me)]\cdot CH_2Cl_2$	Green	93	32.4 (32.2)	4.5 (4.2)	4.6 (4.2)	1 898s	1 620vw

[a] Calculated values in parentheses. [b] Spectra recorded as thin films in $CHCl_3$ between NaCl plates; s = strong, vw = very weak; ν(C≡C) was not observed for complexes **(1)**—**(12)**.

(20) were confirmed as solvates or half solvates by repeated elemental analyses and ^1H n.m.r. spectroscopy. All the compounds are stable in the solid state at 0 °C under nitrogen for several days, however they are much more air-sensitive in solution. The but-2-yne complexes are more soluble than the diphenylacetylene compounds and the ethyl thiocarbonate complexes are much more soluble than their dithiocarbamate analogues. All the complexes **(1)**—**(20)** are soluble in CH_2Cl_2 and $CHCl_3$.

The reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equivalent of $Na[S_2CNEt_2]\cdot 3H_2O$ in $CHCl_3$ was followed by i.r. spectroscopy. The spectrum of the reaction mixture after 10 min shows carbonyl bands at 2 055, 2 045, and 1 895 cm^{-1} which can be assigned to $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$, $[WI(CO)(S_2CNEt_2)(\eta^2\text{-}MeC_2Me)_2]$ and $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$ respectively. After 40 min another carbonyl band at 1 980 cm^{-1} is observed, which increases in intensity over the next 40 min, while the band at 1 895 cm^{-1} decreases in intensity. The band at 1 980 cm^{-1} could be due to the monodentate dithiocarbamate intermediate $[WI(CO)(S_2CNEt_2\text{-}S)(S_2CNEt_2\text{-}SS')(\eta^2\text{-}MeC_2Me)]$ resulting from iodide attack on $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$. Over the next 120 min the bands at 2 055, 1 980, and 1 895 cm^{-1} disappeared leaving only a single carbonyl band at 2 045 cm^{-1} due to complex **(3)**. The proposed mechanism for the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equivalent of $Na[S_2CNEt_2]\cdot 3H_2O$ is shown in Scheme 1. It is interesting that on reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equivalent of $Na[S_2CNEt_2]\cdot 3H_2O$ in CH_2Cl_2 the solution rapidly becomes dark green due to the formation of the bis(dithiocarbamate) compound $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$, whereas the solution obtained in the 1:1 reaction in diethyl ether remains pale yellow-green in colour and hence little of the bis(dithiocarbamate) compound is formed under these conditions. Further evidence to support this mechanism comes from the reaction of $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$ with equimolar quantities of NaI and $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ in CH_2Cl_2 which afforded only the monodithiocarbamate complex $[WI(CO)(S_2CNEt_2)(\eta^2\text{-}MeC_2Me)_2]$. Many attempts were made to isolate the monodentate dithiocarbamate intermediate $[WI(CO)(S_2CNEt_2\text{-}S)(S_2CNEt_2\text{-}SS')(\eta^2\text{-}MeC_2Me)]$ without success.

The structure of complex **(9)** consists of discrete units of

Table 2. Proton n.m.r. data (δ, *J* in Hz)* for the complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ and $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$

Complex	
(1)	3.45, 3.16 (d, 6 H, Me); 2.91, 2.82 (d, 12 H, MeC_2)
(2)	7.35—7.02 (br m, 20 H, PhC_2); 3.22 (br s, 6 H, Me)
(3)	3.83, 3.74 (q, *J* 5.4, 4 H, CH_2); 2.91, 2.82 (d, 12 H, MeC_2); 1.55 (t, *J* 7.2, 6 H, Me)
(4)	7.38 (br m, 20 H, PhC_2); 3.77, 3.66 (q, *J* 5.4, CH_2); 1.26 (t, *J* 7.5, Me)
(5)	7.4—7.27 (br m, 10 H, PhC_2); 5.29 (s, 1 H, CH_2Cl_2); 4.64 (q, *J* 7.2, 4 H, CH_2); 2.95, 2.88 (d, 12 H, MeC_2)
(6)	7.37 (br m, 30 H, Ph); 4.73, 4.61 (q, *J* 7.2, 4 H, CH_2)
(7)	4.73, 4.61 (q, *J* 7.2, 2 H, CH_2); 2.87 (br s, 12 H, MeC_2); 1.51 (t, *J* 7.2, 3 H, Me)
(8)	7.39 (br s, 20 H, Ph); 4.60, 4.49 (q, *J* 6.6, 2 H, CH_2); 1.39 (t, *J* 7.2, 3 H, Me)
(9)	3.71, 3.59 (q, *J* 7.2, 4 H, CH_2N); 2.96, 2.82 (2 s, 12 H, MeC_2); 2.05, 1.99 (q, *J* 3.6, 4 H, CH_2)
(10)	7.25 (br m, 20 H, Ph); 3.74, 3.62 (q, *J* 7.2, 4 H, CH_2N); 2.12, 2.06 (q, *J* 3.6, 4 H, CH_2)
(11)	3.98 (br q, 4 H, CH_2N); 3.26 (br s, 12 H, MeC_2); 1.88 (br m, 6 H, CH_2)
(12)	7.38 (br m, 20 H, Ph); 5.29 (s, 2 H, CH_2Cl_2); 4.11, 3.85 (br q, 4 H, CH_2N); 2.0, 1.8 (br m, 6 H, CH_2)
(13)	3.36 (s, 6 H, MeC_2); 3.24, 3.15 (s, 12 H, Me)
(14)	3.68, 3.56 (q, *J* 7.2, 8 H, CH_2); 3.24 (s, 6 H, MeC_2); 1.36 (t, *J* 3.2, 12 H, Me)
(15)	7.56—7.26 (br m, 10 H, Ph); 3.69, 3.57 (q, *J* 7.2, 8 H, CH_2); 1.25 (t, *J* 3.2, 12 H, Me)
(16)	7.34 (br m, 20 H, Ph); 5.30 (s, 1 H, CH_2Cl_2); 4.85, 4.73 (q, *J* 7.2, 8 H, CH_2); 3.34 (s, 3 H, MeC_2); 2.97 (s, 3 H, C_2Me)
(17)	4.74, 4.62 (q, *J* 7.2, 8 H, CH_2); 3.00 (s, 6 H, MeC_2); 1.5 (t, *J* 7.8, 12 H, Me)
(18)	7.35 (br m, 10 H, Ph); 4.62, 4.49 (q, *J* 7.7, 4 H, CH_2); 1.41 (t, *J* 7.2, 6 H, Me)
(19)	3.69, 3.57 (q, *J* 7.2, 8 H, CH_2N); 3.24 (s, 6 H, MeC_2); 2.03, 1.97 (q, *J* 5.6, 8 H, CH_2)
(20)	5.31 (s, 2 H, CH_2Cl_2); 3.94 (br q, 8 H, CH_2N); 3.25 (s, 6 H, MeC_2); 1.85 (br m, 12 H, CH_2)

* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; br = broad, d = doublet, m = multiplet, q = quartet, and t = triplet.

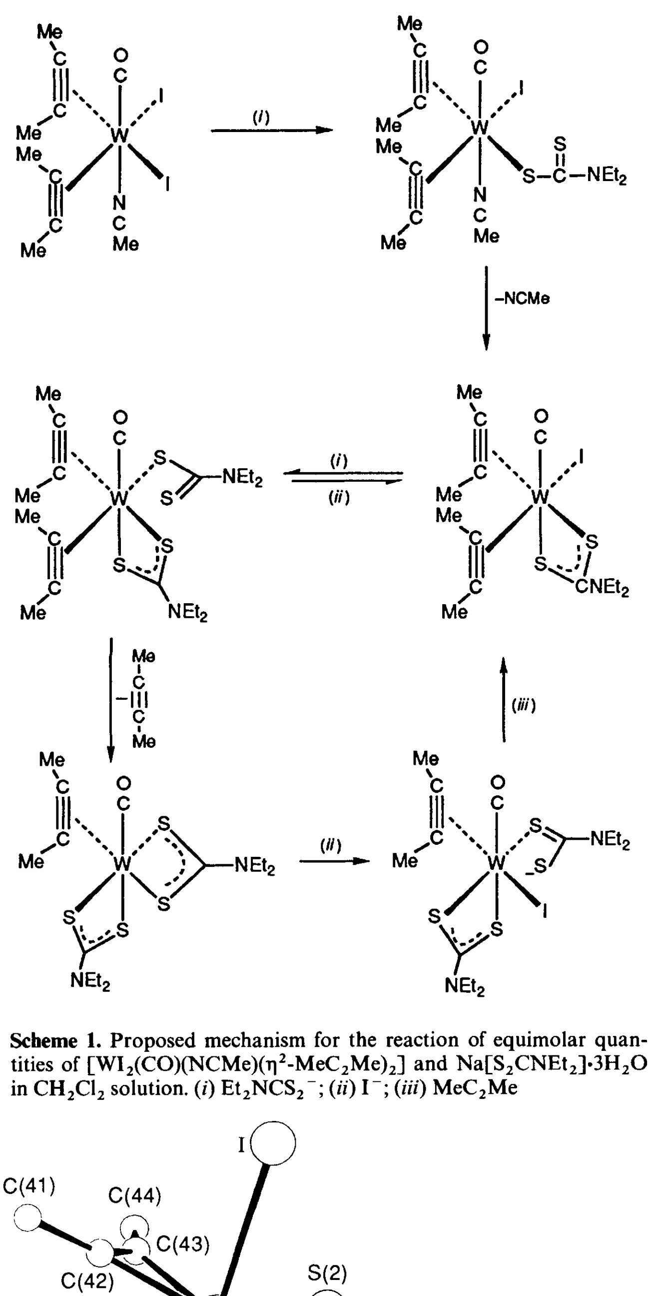
Table 3. ^{13}C N.m.r. data* (δ/p.p.m.) for selected complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ and $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$

Complex	
(1)	209.08 (s, CO); 207.26 (s, CS_2); 178.6, 156.11 (s, C≡C); 40.02 (s, Me); 39.37, 39.11 (d, *Me*C_2)
(4)	205.75 (s, CO); 202.52 (s, CS_2); 189.73, 145.28 (s, C≡C); 139.17 (s, *i-Ph*C_2); 131.25 (m, *o*-Ph); 128.13 (m, *m*-Ph); 126.31 (s, *p*-Ph); 44.05 (s, CH_2); 12.52, 12.34 (d, Me)
(5)	208.96, 208.70 (d, CO); 203.73 (s, CS_2); 185.3, 167.62 (s, C≡C); 133.98, 133.46 (d, *i-Ph*C); 128.65 (s, *o*-Ph); 128.39 (s, *m*-Ph); 127.82 (s, *p*-Ph); 56.07 (s, CH_2Cl_2); 50.42, 50.16 (d, CH_2); 18.97, 16.24 (d, *Me*C_2)
(7)	205.75 (s, CO); 205.84 (s, CS_2); 156.40 (s, C≡C); 45.35, 44.31 (d, CH_2); 29.63 (*Me*C_2); 12.86 (s, Me)
(8)	205.75 (s, CO); 202.52 (s, CS_2); 189.73 (s, C≡C); 139.17 (s, *iPh*C_2); 133.33 (s, *o*-Ph), 131.25 (s, *p*-Ph), 128.31 (s, *m*-Ph); 44.05 (s, CH_2); 12.57 (s, Me)
(9)	204.14 (s, CO); 197.26 (s, CS_2); 162.31, 151.39 (s, C≡C); 44.31 [s, CH_2 (*o*-N)]; 24.56 (s, *Me*C_2); 19.62, 14.03 (s, CH_2)
(11)	197.39 (s, CO); 195.89 (s, CS_2); 175.26, 148.41 (s, C≡C); 48.86 [s, CH_2 (*o*-N)]; 44.57 [s, CH (*m*-N)]; 25.6 [s, CH_2 (*p*-N)]; 21.96 (s, *Me*C_2)
(13)	237.41 (s, CO); 213.5; 211.82 (s, C≡C); 201.68 (s, CS_2); 40.67, 39.37 (s, Me); 20.4 (s, *Me*C_2)
(14)	211.94, 210.76 (s, C≡C); 200.24 (s, CO); 194.26 (s, CS_2); 45.74, 43.92 (s, CH_2); 20.0 (s, *Me*C); 12.47 (s, Me)
(15)	212.6 (s, C≡C); 208.85 (s, CO); 204.73 (s, CS_2); 139.56 (s, *Ph*C_2); 128.65—128.39 (br m, Ph); 45.74, 43.92 (s, CH_2); 12.21 (s, Me)
(17)	227.53 (s, CO); 207.78 (s, C≡C); 178.93 (s, CS_2); 67.57 [s, CH_2 (S_2COEt)]; 29.63 (s, *Me*C_2); 19.88, 17.28, 16.1 [m, CH_2 (OEt)]; 13.77 [s, Me (S_2COEt)]; 4.94 [s, Me (OEt)]
(19)	238.07 (s, CO); 211.82; 207.66 (s, C≡C); 197.26 (s, CS_2); 50.55, 49.64, 49.38 [m, CH_2 (*o*-N)]; 24.82 (s, CH_2); 20.77 (s, *Me*C_2)

* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; s = singlet, m = multiplet, and d = doublet.

$[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ and the molecule is shown in Figure 1 together with the atomic numbering scheme. The tungsten atom is bonded to one iodine atom [W–I 3.005(1)], two sulphur atoms of the dithiocarbamate ligand [W–S(1) 2.500(5) and 2.530(5)], one carbonyl group [W–C(20) 2.009(22)], and two alkynes [W–C(32) 2.080(20), W–C(33) 2.104(19); and W–C(42) 2.078(19), W–C(43) 2.103(17) Å]. The geometry around the tungsten atom is best considered as distorted octahedral with the alkynes each occupying one site in the co-ordination sphere. The carbonyl group is *trans* to S(2) while alkynes are *trans* to S(1) and I. Thus, as is common in d^4 systems, both alkyne moieties are parallel to the M–CO axis (Figure 1),[4–6,11,16,17] a configuration which optimises both the π-donor and π-acceptor roles of the alkyne ligand. The bond lengths from tungsten are as expected from previous structures though somewhat on the long side; in particular W–I is significantly longer than that found in previous structures (*i.e.* 2.809(2) and 2.829(2) in $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$,[17] 2.843(1) and 2.859(1) in $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$,[16] and 2.848(1) and 2.862(2) Å in $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$[16]). However, these previous structures contain predominantly monodentate ligands and the increased bond length in the present molecule may well be due to increased steric crowding caused by the additional bidentate dithiocarbamate. It is particularly noticeable that I subtends several angles of less than 90° at the metal with adjacent atoms. The equatorial plane containing atoms S(1), S(2), C(20), and CM(4) [midpoint of the C(42)–C(43) bond] is planar to within 0.04 Å with the metal atom 0.29 Å out of the plane away from the iodine atom and towards CM(3) [midpoint of the C(32)–C(33) bond]. The alkyne group C(41), C(42), C(43), and C(44) intersects this equatorial plane at 16.9°. The C(41)–C(42)–C(43) angle at 143(2)° is significantly less than C(42)–C(43)–C(44) of 153(2)°. This reflects steric interaction between C(41) and the adjacent carbonyl group CO(20). A smaller difference is observed for C(32)–C(33)–C(34) 147(2)° and C(31)–C(32)–C(33) 141(2)° but here it may well be that interaction with S(2) causes the disparity.

In the dithiocarbamate ligand the five-membered ring is puckered with successive internal torsion angles around the bonds of N(4)–C(5) −12.8, C(5)–C(6) 30.1, C(6)–C(7) −37.3, C(7)–C(8) 29.1, and C(8)–N(4) −10.4°. The remaining dimen-



Scheme 1. Proposed mechanism for the reaction of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and $Na[S_2CNEt_2]\cdot 3H_2O$ in CH_2Cl_2 solution. (*i*) $Et_2NCS_2^-$; (*ii*) I^-; (*iii*) MeC_2Me

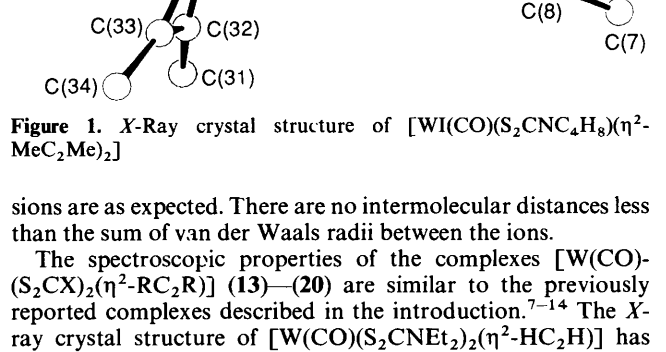


Figure 1. *X*-Ray crystal structure of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$

sions are as expected. There are no intermolecular distances less than the sum of van der Waals radii between the ions.

The spectroscopic properties of the complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ (**13**)—(**20**) are similar to the previously reported complexes described in the introduction.[7–14] The *X*-ray crystal structure of $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ has been determined[11] and it is highly likely that the structure of (**13**)—(**20**) is similar (Figure 2).

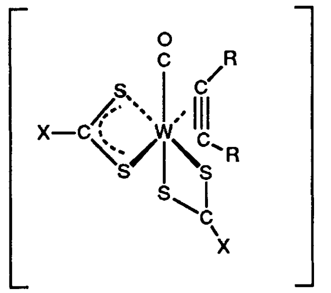
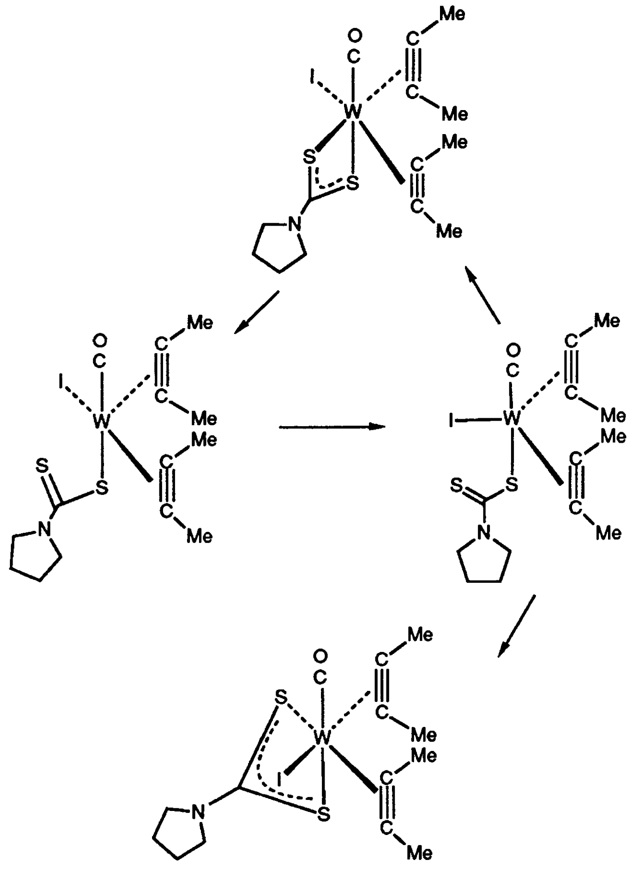


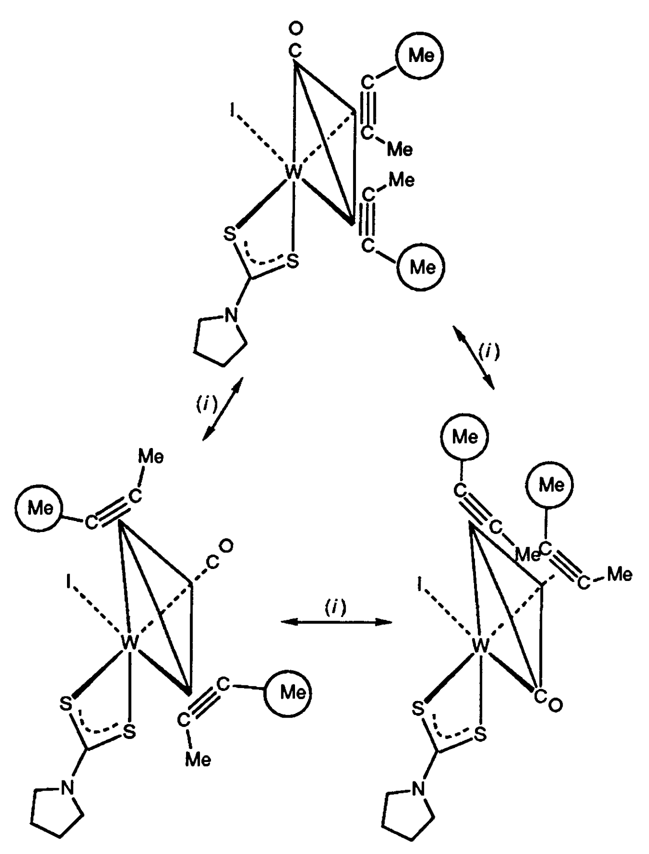
Figure 2. Proposed structure of the complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$

The i.r. spectra of the complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ (**1**)—(**12**) all show a high carbonyl band well above 2 000 cm^{-1} (Table 1). This is not surprising since the two alkyne ligands are good π acceptors and hence there is little electron density on the metal for back donation to the π* orbitals of the carbonyl ligand. As expected the monoalkyne complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ (**13**)—(**20**) show much lower carbonyl-stretching bands ($\approx$1 900 cm^{-1}) since they contain two electron-rich anionic sulphur-donor ligands. The weak alkyne (C≡C) stretching bands are all considerably lower than for the 'free' alkyne ligand for complexes (**13**)—(**20**) which is expected as there is considerable back donation into the π* orbitals of the alkyne ligand in these compounds.

The room-temperature ^1H n.m.r. spectra of (**1**)—(**12**) show only two different but-2-yne methyl environments, which might suggest a symmetric structure with the but-2-yne ligands *trans* to the two sulphur atoms of the dithiocarbamate ligands, however variable-temperature ^1H n.m.r. studies carried out on complex (**9**) indicate that a rapid fluxional process is occurring at room temperature. The spectrum at room temperature shows two singlets for the but-2-yne methyl groups at δ 2.82 and 2.96. On cooling the solution the two singlets collapse to two separate doublets with coalescence temperatures of T_c = 243 and 233 K, which have separations (Δv) of 23 and 5.94 Hz respectively. The calculated[18,19] free energies of activation for the two separate signals undergoing collapse are $\Delta G^{\ddagger}_{T_c}$ = 51.2 and 50.9 kJ mol^{-1}, *i.e.* the same within experimental error. Davidson and Vasapollo[15] studied the fluxionality of the closely related bis(but-2-yne) dimethyldithiocarbamate complex $[WBr(CO)(S_2CNMe_2)(\eta^2\text{-}MeC_2Me)_2]$, and they found similarly that the two singlet but-2-yne resonances at room temperature underwent collapse on cooling to give two pairs of doublets with similar values for the free energy of activation. They suggested that the complex was more likely to be undergoing a dechelation mechanism as shown in Scheme 2, and considered that if the two but-2-yne ligands were undergoing independent but-2-yne rotation they would be unlikely to have the same barrier to such rotation as for the asymmetric structure shown in Figure 1. However, the possibility of a trigonal twist mechanism was considered unlikely since they believed that it was not possible to exchange the but-2-yne ligands through a single trigonal twist without carbon monoxide becoming *trans* to but-2-yne which is a highly unfavourable configuration. However, we consider it is possible for the molecule to undergo a simple trigonal twist to exchange the but-2-yne ligands as shown in Scheme 3 for complex (**9**). Hence at room temperature (**9**) is undergoing either (*i*) dechelation of the dithiocarbamate ligand which exchanges the but-2-yne methyl groups as shown in Scheme 2 or (*ii*) a rapid trigonal twist rearrangement as shown in Scheme 3, which again exchanges the methyl groups. It is difficult to distinguish between these two processes, however it might be expected that a simple trigonal twist should be a lower-energy process compared to a bond-dissociation process.



Scheme 2. Dechelation mechanism proposed by Davidson and Vasapollo[15] shown for $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ (**9**)



Scheme 3. Our proposed trigonal twisting [(*i*)] equilibration mechanism of the co-ordinated but-2-yne ligands in $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ (**9**)

Hence, in contrast to Davidson and Vasapollo[15] we tend to favour a trigonal twist mechanism. The ^1H n.m.r. spectra of the but-2-yne methyl protons for the bis(dithiocarbamate) complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}MeC_2Me)]$ all show a single resonance at room temperature except where $X = N(CH_2Ph)_2$ which suggests that rapid propeller-like rotation of the but-2-yne is occurring at room temperature, but for the more bulky dibenzyldithiocarbamate complex (**16**) the fluxional process is slowed down significantly to see two separate methyl resonances (see Table 2). This fluxional process for other bis(dithiocarbamate) monoalkyne complexes of molybdenum(II) and tungsten(II) has been previously observed.[12,13] It should be noted that we are currently carrying out further variable-temperature n.m.r. studies on complexes closely related to those described in this paper in order further to elucidate the fluxional processes involved.

Alkyne complexes have the ability to donate between two and four electrons to a transition metal. This has been studied by both (*a*) theoretical calculations[20–22] and (*b*) experimental results.[23–25] Ward and Templeton[26] have correlated the number of electrons donated by an alkyne to the ^{13}C n.m.r. alkyne contact-carbon resonances. The complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ (**1**)—(**12**) all show alkyne contact-carbon resonances between 145.28 and 189.73 p.p.m. These values suggest that the alkyne ligands are donating an average of three electrons each to the tungsten. This is consistent with the complexes obeying the effective atomic number rule. The monoalkyne complexes $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ (**13**)—(**20**), however, have alkyne contact-carbon shifts above 200 p.p.m. which indicates that the alkyne ligands are donating four electrons to the tungsten. This would be expected if the complexes obey the effective atomic number rule. It is interesting that complexes (**13**)—(**20**) are all highly coloured which has been previously observed[4,5,13,17,23,25] for complexes with monoalkyne ligands donating four electrons to the metal, whereas complexes (**1**)—(**12**) with three-electron alkyne ligands are mainly yellow or brown (Table 1), similar to other 'three-electron' alkyne complexes.[2,4,6,15,16]

Experimental

All reactions were carried out using standard Schlenk-line techniques. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) were prepared by the literature method.[16] It should be noted that the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) sometimes analyse as a $0.5CH_2Cl_2$ solvate (as shown by the *X*-ray crystal structures[16]) or as non-solvates, usually when in powder form and hence both forms have been used in the reactions described in this paper. The ligands $Na[S_2CNMe_2]\cdot 2H_2O$, $Na[S_2CNEt_2]\cdot 3H_2O$, $K[S_2COEt]$, and $[NH_4][S_2CNC_4H_8]$ were purchased from commercial sources; $K[S_2CNC_5H_{10}]$ was prepared by the literature method.[27] Dichloromethane was dried over P_2O_5. I.r. spectra were recorded as thin films in $CHCl_3$ between NaCl plates on a Perkin-Elmer 197 spectrophotometer, ^1H and ^{13}C n.m.r. spectra on a JEOL FX 60, a Bruker AC 250 CP/MAS, or a Bruker WH 400-MHz spectrometer (all spectra were calibrated against tetramethylsilane). Elemental analyses for carbon, hydrogen, and nitrogen were determined using a Carlo Erba Analyser MOD 1106 (with helium as a carrier gas).

Table 4. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for complex (**9**)

Atom	*x*	*y*	*z*
W	1 860(1)	1 622(0)	4 357(1)
I	2 566(2)	3 211(1)	5 127(1)
S(1)	748(5)	1 606(3)	6 426(4)
S(2)	3 674(5)	1 171(3)	5 936(5)
C(3)	2 329(18)	1 249(9)	6 977(19)
N(4)	2 445(16)	1 022(9)	8 112(14)
C(5)	3 754(19)	668(12)	8 672(19)
C(6)	3 476(24)	697(17)	10 028(22)
C(7)	1 805(22)	646(13)	10 095(19)
C(8)	1 261(22)	1 106(11)	9 006(18)
C(20)	103(25)	2 184(11)	3 764(20)
O(20)	−904(16)	2 497(9)	3 418(14)
C(31)	2 491(29)	−229(12)	3 935(27)
C(32)	1 685(23)	472(11)	3 984(22)
C(33)	549(24)	776(11)	3 576(17)
C(34)	−870(24)	665(13)	2 950(23)
C(41)	2 093(21)	2 563(11)	1 676(19)
C(42)	2 547(21)	2 063(10)	2 703(17)
C(43)	3 624(19)	1 740(12)	3 175(17)
C(44)	5 155(21)	1 521(14)	3 202(27)

Table 5. Dimensions (distances in Å, angles in°) in the co-ordination sphere

W–I	3.005(1)	W–C(32)	2.080(20)
W–S(1)	2.500(5)	W–C(33)	2.104(19)
W–S(2)	2.530(5)	W–C(42)	2.078(19)
W–C(20)	2.009(22)	W–C(43)	2.103(17)
I–W–S(1)	81.15(12)	C(32)–W–C(33)	35.0(8)
I–W–S(2)	87.78(12)	I–W–C(42)	80.02(46)
S(1)–W–S(2)	69.58(15)	S(1)–W–C(42)	158.1(5)
I–W–C(20)	78.6(5)	S(2)–W–C(42)	120.6(5)
S(1)–W–C(20)	87.8(6)	C(20)–W–C(42)	77.6(8)
S(2)–W–C(20)	155.2(6)	C(32)–W–C(42)	102.7(7)
I–W–C(32)	170.4(5)	C(33)–W–C(42)	95.3(6)
S(1)–W–C(32)	97.7(6)	I–W–C(43)	85.0(5)
S(2)–W–C(32)	82.9(6)	S(1)–W–C(43)	152.6(5)
C(20)–W–C(32)	111.0(7)	S(2)–W–C(43)	86.5(5)
I–W–C(33)	154.5(6)	C(20)–W–C(43)	112.5(8)
S(1)–W–C(33)	96.9(5)	C(32)–W–C(43)	92.0(8)
S(2)–W–C(33)	115.5(5)	C(33)–W–C(43)	105.5(7)
C(20)–W–C(33)	76.0(7)	C(42)–W–C(43)	35.0(7)

[WI(CO)(S$_2$CNC$_4$H$_8$)(η^2-MeC$_2$Me)$_2$] (**9**).—In a typical reaction [NH$_4$][S$_2$CNC$_4$H$_8$] (0.250 g, 1.522 mmol) was added to a stirring solution of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·0.5CH$_2$Cl$_2$ (1.0 g, 1.521 mmol) in CH$_2$Cl$_2$ (30 cm^3). After 17 h the solution was filtered and dried *in vacuo*. Dichloromethane (3 cm^3) was added to the crude product which was then transferred to a 10-cm anaerobic silica column. The product was eluted with diethyl ether yielding two bands, one green band corresponding to [W(CO)(S$_2$CNC$_4$H$_8$)$_2$(η^2-MeC$_2$Me)] (**19**) and a yellow band of [WI(CO)(S$_2$CNC$_4$H$_8$)(η^2-MeC$_2$Me)$_2$] (**9**). Once all complex (**19**) was collected the eluant was changed to CH$_2$Cl$_2$ and complex (**9**) was collected. Recrystallisation of (**19**) from diethyl ether yielded 0.05 g (6%), and (**9**) from CH$_2$Cl$_2$–Et$_2$O yielded 0.53 g (58%).

Similar reactions of [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$]·0.5CH$_2$Cl$_2$ (R = Me and Ph) with 1 equivalent of Na[S$_2$CNMe$_2$]·2H$_2$O, Na[S$_2$CNEt$_2$]·3H$_2$O, Na[S$_2$CN(CH$_2$Ph)$_2$], K[S$_2$COEt], [NH$_4$][S$_2$CNC$_4$H$_8$], or K[S$_2$CNC$_5$H$_{10}$] in CH$_2$Cl$_2$ at room temperature gave the new complexes (**1**)—(**8**) and (**10**)—(**12**) (see Table 1 for physical and analytical data).

Complex (**9**) could also be prepared by an alternative method. In a typical reaction [NH$_4$][S$_2$CNC$_4$H$_8$] (0.250 g, 1.522 mmol) was added to a stirring suspension of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·0.5CH$_2$Cl$_2$ (1.000 g, 1.521 mmol) in diethyl ether (30 cm^3). After 17 h the solution was syringed off if it had a green colouration and washed with further portions (10 cm^3) of diethyl ether until all trace amounts of [W(CO)(S$_2$CNC$_4$H$_8$)$_2$(η^2-MeC$_2$Me)] (**19**) that had formed were removed. The crude product was then dissolved in CH$_2$Cl$_2$ and filtered to remove NH$_4$I. The solvent was then removed *in vacuo* affording a golden solid [WI(CO)(S$_2$CNC$_4$H$_8$)(η^2-MeC$_2$Me)$_2$] (**9**) which was recrystallised from CH$_2$Cl$_2$ and diethyl ether at −25 °C for 24 h to afford single crystals for *X*-ray crystallography, yield 0.82 g, 90%.

Similar reactions of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·0.5CH$_2$Cl$_2$ with an equimolar quantity of Na[S$_2$CNMe$_2$]·2H$_2$O, Na[S$_2$CNEt$_2$]·3H$_2$O, Na[S$_2$CN(CH$_2$Ph)$_2$], or K[S$_2$COEt] in Et$_2$O at room temperature gave the complexes (**1**), (**3**), (**5**), and (**7**).

[W(CO)(S$_2$CNEt$_2$)$_2$(η^2-MeC$_2$Me)] (**14**).—In a typical reaction Na[S$_2$CNEt$_2$]·3H$_2$O (0.396 g, 1.758 mmol) was added to a stirred solution of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (0.520 g, 0.846 mmol) in CH$_2$Cl$_2$ (30 cm^3). The mixture was filtered after 8 h, and solvent removal *in vacuo* afforded a green solid [W(CO)(S$_2$CNEt$_2$)$_2$(η^2-MeC$_2$Me)] (**14**) which was recrystallised from CH$_2$Cl$_2$. Yield of pure product 0.35 g (73%).

Similar reactions of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] with 2 equivalents of Na[S$_2$CNMe$_2$]·2H$_2$O, Na[S$_2$CN(CH$_2$Ph)$_2$], K[S$_2$COEt], [NH$_4$][S$_2$CNC$_4$H$_8$], or K[S$_2$CNC$_5$H$_{10}$] gave the complexes [W(CO)(S$_2$CX)$_2$(η^2-MeC$_2$Me)] (**13**), (**16**), (**17**), (**19**), and (**20**) (see Table 1 for physical and analytical data).

[W(CO)(S$_2$CNEt$_2$)$_2$(η^2-PhC$_2$Ph)] (**15**).—In a typical reaction Na[S$_2$CNEt$_2$]·3H$_2$O (0.160 g, 0.710 mmol) was added to a stirring solution of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (0.300 g, 0.348 mmol) in CH$_2$Cl$_2$ (15 cm^3). After 4 h the mixture was filtered to remove NaI and the solvent was removed *in vacuo* yielding a saturated green solution, which was passed down a 5 cm long anaerobic silica column. Light petroleum (b.p. 60—80 °C) was passed down the column for 30 min to remove PhC$_2$Ph before the eluant was changed to CH$_2$Cl$_2$, and the green band collected. Solvent was removed *in vacuo* and the green product [W(CO)(S$_2$CNEt$_2$)$_2$(η^2-PhC$_2$Ph)] (**15**) was recrystallised from CH$_2$Cl$_2$. Yield of pure product 0.11 g (46%).

In a similar reaction and work-up procedure of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] with 2 equivalents of K[S$_2$COEt] in CH$_2$Cl$_2$ the new compound [W(CO)(S$_2$COEt)$_2$(η^2-PhC$_2$Ph)] (**18**) was obtained (see Table 1 for physical and analytical data).

Crystallography for Complex (**9**).—Crystals of complex (**9**) were prepared as described above.

Crystal data. C$_{14}$H$_{20}$INOS$_2$W, M = 593.0, space group $P2_1/n$, a = 9.256(8), b = 17.685(14), c = 10.962(11) Å, β = 90.5(1)°, U = 1 794.3 Å^3, D_m = 2.23 g cm^{-3}, Z = 4, D_c = 2.19 g cm^{-3}, $F(000)$ = 1 112, λ = 0.7107 Å, μ = 87.65 cm^{-1}.

A crystal of approximate size 0.25 × 0.3 × 0.3 mm was set up to rotate about the *a* axis on a Stoe Stadi 2 diffractometer and data were collected *via* a variable-width ω scan mode and using graphite-monochromatised Mo-K_α radiation. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 2 781 Independent reflections were measured of which 2 097 with $I > 3\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied.[28] The structure was determined by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were refined as rigid groups.

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.061 ($R' = 0.067$). In the final cycle of refinement all shift/error ratios were $< 0.3\sigma$. The final difference Fourier map showed no peaks greater than 1.5 e Å^{-3}. Calculations were carried out using SHELX 76[29] and some of our own programs on the Amdahl V7 computer at the University of Reading. Positional parameters are given in Table 4 and molecular dimensions in the co-ordination sphere in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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