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COUPLING OF CYCLOOCTYNE WITH CARBON MONOXIDE ON DIVALENT MOLYBDENUM AND TUNGSTEN. CRYSTAL AND MOLECULAR STRUCTURE OF A BIS(HEXAMETHYLENE)CYCLOPENTADIENONETUNGSTEN COMPLEX, $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$

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Summary

Cyclooctyne (C_8H_{12}) in excess reacts with the dialkyldithiocarbamato complexes $M(S_2CNR_2)_2(CO)_2L$ (R = Me, Et; M = Mo, L = PPh_3; M = W, L = CO, PPh_3) to give a mixture of two complexes, $M(S_2CNR_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**1–4**) and $M(S_2CNR_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**5–8**). These contain *tetrahapto*-bis(hexamethylene)cyclopentadienone, $(C_8H_{12})_2CO$, formed by the condensation of two molecules of cyclooctyne with one molecule of CO. Crystals of $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**3**) are monoclinic, space group $P2_1/n$, with *a* 15.132(1), *b* 15.705(2), *c* 11.346(1) Å, β 93.68(2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares methods to $R = 0.027$ ($R_w = 0.045$) for 5811 unique data [$I \geq 3\sigma(I)$]. The molecule is approximately pentagonal bipyramidal, with terminal CO and one sulphur atom of a bidentate Me_2NCS_2 ligand in the axial positions. The equatorial sites are occupied by the other sulphur atom of this Me_2NCS_2 ligand, the second bidentate Me_2NCS_2 ligand, and the mid-points of the coordinated C=C bonds of η^4-$(C_8H_{12})_2CO$. As in other cyclopentadienone complexes, the C=C distances in the η^4-dienone are almost equal (av. 1.45 Å) and the C=O group is bent away from the plane of the ring (dihedral angle 17.6°). Infrared and NMR (^1H, ^{13}C) data suggest that complexes **5–8** are similar to **1–4**, with cyclooctyne acting as a 2π-electron donor in place of CO.

Introduction

In the preceding paper [1], we showed that dialkyldithiocarbamato (dtc) complexes of molybdenum and tungsten, $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ and $W(S_2CNR_2)_2(CO)_2L$ (R = Me, Et; L = CO, PPh_3), react with cyclooctyne (C_8H_{12})

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in a 1/1 mol ratio to give green, crystalline complexes of formula $M(S_2CNR_2)_2(CO)(C_8H_{12})$ in which cyclooctyne appears to act as a 4π-electron donor. We noted the necessity to keep the reactant ratio close to 1/1 because of further reaction with cyclooctyne and in this paper we describe the products formed when an excess of cyclooctyne is present.

Results

When two or more mol equivs. of cyclooctyne are added at room temperature to $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ or $W(S_2CNR_2)_2(CO)_2L$ ($L = CO, PPh_3$), a mixture of two orange-yellow, microcrystalline complexes is formed (eq. 1).

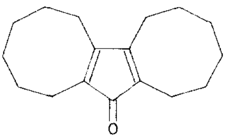
$$M(S_2CNR_2)_2(CO)_2L + C_8H_{12}\ (\text{excess}) \rightarrow$$

$$(M = Mo,\ L = PPh_3;\quad M = W,\ L = CO,\ PPh_3)$$

$$M(S_2CNR_2)_2(CO)\{(C_8H_{12})_2CO\} + M(S_2CNR_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\} + L \quad (1)$$

$(M = Mo,\ R = Me$ (**1**);	$(M = Mo,\ R = Me$ (**5**);
$M = Mo,\ R = Et$ (**2**);	$M = Mo,\ R = Et$ (**6**);
$M = W,\ R = Me$ (**3**);	$M = W,\ R = Me$ (**7**);
$M = W,\ R = Et$ (**4**))	$M = W,\ R = Et$ (**8**))

These complexes have the general formulae $M(S_2CNR_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**1**–**4**) and $M(S_2CNR_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**5**–**8**), both containing bis(hexamethylene)cyclopentadienone, $(C_8H_{12})_2CO$ (I), formed by condensation of two molecules of cyclooctyne with one of carbon monoxide. The two types differ only in the replacement of terminal CO in **1**–**4** by cyclooctyne in **5**–**8**. In most cases we have been able to separate one component of the mixture by fractional crystallization. The relative amounts of the two types of complex formed in the reaction depend on the metal, on the alkyl group of the R_2NCS_2 ligand, and on the conditions. Thus, for M = W and R = Me, **3** predominates over **7**, whereas for M = Mo and R = Me, **5** predominates over **1**, consistent with the usual trend that CO is more easily replaced from molybdenum than from tungsten. For the diethyldithiocarbamates (R = Et), the cyclooctyne complexes **6** and **8** are the major products for M = Mo and W, although fortuitously the carbonyl complex **4** can be isolated in a pure state from the reaction of $W(S_2CNEt_2)_2(CO)_2(PPh_3)$ with cyclooctyne. The general trend correlates with the observation that the diazoalkane complexes $W(CO)(N_2CR'_2)(S_2CNR_2)_2$ ($R = Me, Et$; R' = various aryl groups) lose CO more readily when R = Et than when R = Me, a fact which has been attributed to the greater electron-donating ability of the Me_2NCS_2 ligand [2].



I

The proportion of carbonyl complexes **1**–**4** is increased by performing the reaction under CO and **1** can be isolated in a pure state under these conditions. Conversely, if the ratio of CO to C_8H_{12} is reduced by using $M(S_2CNR_2)_2(CO)(C_8H_{12})$ as starting material, the proportion of the cyclooctyne complexes is increased and pure **7** was isolated in this way. The carbonyl complexes **1**–**4** do not react with an excess of cyclooctyne to give **5**–**8** and are not formed from **5**–**8** by reaction with CO.

Spectroscopic data

The IR spectra of all the complexes exhibit a $\nu(C\overset{..}{-}N)$ band at ca. 1500 cm^{-1} and an intense band at ca. 1600 cm^{-1} due to the C=O group of I (Table 1). Additional bands appear at ca. 1930 cm^{-1} due to $\nu(C\equiv O)$ in the IR spectra of the carbonyl complexes **1**–**4** and at ca. 1830–1870 cm^{-1} due to $\nu(C\equiv C)$ modified by coordination in the spectra of the cyclooctyne complexes **5**–**8**. The $\nu(C\equiv O)$ frequencies for **1**–**4** are significantly higher than those of the precursors $M(S_2CNR_2)_2(CO)(C_8H_{12})$ (ca. 1900 cm^{-1}) [1], indicating that bis(hexamethylene)cyclopentadienone is a stronger π-acceptor than cyclooctyne. The $\nu(C\equiv O)$ value for the dimethyldithiocarbamato complex **3** is ca. 10 cm^{-1} lower than that for its diethyldithiocarbamato analogue **4** and, conversely, the $\nu(C\overset{..}{-}N)$ values for the corresponding pairs **3**/**4**, **5**/**6** and **7**/**8** are always in the order $Me_2NCS_2 > Et_2NCS_2$. Similar observations have been made for the diazoalkane complexes mentioned above [2]. The $\nu(C\equiv O)$ value for the tungsten complex **3** is ca. 10 cm^{-1} to lower frequency than that of its molybdenum analogue **1**, as is true also for the $M(S_2CNR_2)_2(CO)(C_8H_{12})$ complexes [1]. Similarly, the $\nu(C\equiv C)$ values for the cyclooctyne tungsten complexes **7** and **8** are ca. 20–30 cm^{-1} to lower frequency than those of the corresponding molybdenum complexes **5** and **6**. These observations reflect the stronger bonding of the CO or C_8H_{12} ligands to the third row element.

Most of the complexes do not show parent ions in their mass spectra. The most intense peak is at *m/z* 244 due to bis(hexamethylene)cyclopentadienone (I), an observation which first suggested the presence of this ligand in the complexes. A corresponding peak is also found in the mass spectra of *tetrahapto*-cyclopentadienone complexes of molybdenum and tungsten such as $MoCl(\eta\text{-}C_5H_5)(CO)\{C_4(CF_3)_4CO\}$, $WCl(\eta\text{-}C_5H_5)(CO)(C_4Me_2Ph_2CO)$ and $Mo(SCF_3)(\eta\text{-}C_5H_5)(CO)\{C_4H_2(CF_3)_2CO\}$ [3]. Other fragments observed in the mass spectra of complexes **1**–**8** correspond to the loss of one and two CO groups, C_8H_{12}, and $(C_8H_{12})_2CO$. The most intense metal-containing fragment is $[M(S_2CNR_2)_2]^+$.

The most definitive spectroscopic information about the complexes comes from their $^{13}C\{^1H\}$ NMR spectra (Table 2). The fact that there are two absorptions for the trigonal carbon atoms of the dtc ligands and four absorptions for the carbon atoms of the alkyl substituents shows that the dtc ligands are inequivalent and do not interconvert rapidly on the NMR time scale. The cyclopentadienone ring in each compound gives rise to a maximum of four signals in the region δ 88–108 ppm due to the inequivalent olefinic carbon atoms and a singlet at δ ca. 170 ppm due to the ketonic carbon atom. Peaks in these regions have been observed and similarly assigned in the $^{13}C\{^1H\}$ NMR spectra of the tetrakis(alkyl)- or tetrakis(aryl)-cyclopentadienone complexes $Fe(CO)_3(\eta^4\text{-}C_4R_4CO)$ (R = Ph, CF_3; M = Fe, Ru) [4] and $M(\eta\text{-}C_5H_5)(C_4Et_4CO)$ (M = Co, Rh) [5]. The appearance of four olefinic carbon resonances in our complexes shows that there is no perpendicular plane of symmetry

(Continued on p. 186)

TABLE 1

^{1}H NMR AND SELECTED IR DATA FOR BIS(HEXAMETHYLENE)CYCLOPENTADIENONE COMPLEXES OF MOLYBDENUM AND TUNGSTEN [a]

Complex	^{1}H NMR (δ) [b]			IR (cm^{-1}) [c]
	CH_3(dtc)	CH_2(dtc)	$CH_2(C_8H_{12})$	
$Mo(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**1**)	3.36s, 3.30s 3.23s, 3.13s [d]		2.9–2.6 br m, 2.2–1.4 br m	1932(C≡O), 1626(C=O), 1525(C$\overset{\cdots}{-}$N)
$W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**3**)	3.24s, 3.22s, 3.21s [e]		2.8–2.4 br m, 2.1–1.3 br m	1921(C≡O), 1623(C=O), 1530(C$\overset{\cdots}{-}$N)
$W(S_2CNEt_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**4**)	1.3–1.1 m	3.7–3.5 m	2.6–1.1 br m	1930(C≡O), 1614(C=O), 1513, 1503(C$\overset{\cdots}{-}$N)
$Mo(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**5**)	3.31s, 3.28s, 3.18s, 3.06s [d]		2.9–2.6 br m, 2.2–1.4 br m	1858(C≡C), 1597(C=O), 1518(C$\overset{\cdots}{-}$N)
$Mo(S_2CNEt_2)_2(C_8H_{12})\{C_8H_{12})_2CO\}$ (**6**)	1.32–1.06 m	4.0–3.35 m	2.7–1.1 br m	1870(C≡C), 1595(C=O), 1488(C$\overset{\cdots}{-}$N)
$W(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**7**)	3.31s, 3.17s, 3.06s [e]		2.8–2.4 br m, 2.1–1.3 br m	1835(C≡O), 1596(C=O), 1524(C$\overset{\cdots}{-}$N)
$W(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**8**)	1.45–1.0 m	4.3–3.3 br m	3.1–1.0 br m	1835(C≡C), 1585(C=O), 1495(C$\overset{\cdots}{-}$N)

[a] Abbreviations: s, singlet; m, multiplet; br, broad. [b] Measured in $CDCl_3$. [c] Measured in Nujol mulls. [d] Intensity ratio 1/1/1/1. [e] Intensity ratio 2/1/1.

TABLE 2

^{13}C NMR DATA (δ) FOR BIS(HEXAMETHYLENE)CYCLOPENTADIENONE COMPLEXES OF MOLYBDENUM AND TUNGSTEN [a,b]

Complex	C≡O or C≡C	R_2NCS_2	C=O	C=C	CH_3(dtc)	CH_2(dtc)
$W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**3**)	221.4(C≡O)	216.0, 205.4	168.9	94.3, 92.4 92.0, 88.9	39.76, 39.11, 38.85, 38.59	
$W(S_2CNEt_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**4**)	222.7(C≡O)	214.2, 204.2	170.0	94.3, 93.7, 92.9, 88.7	12.54, 12.28	45.42, 44.52, 44.40, 44.31
$Mo(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**5**)	127.7, 120.5(C≡C)	208.8, 204.8	169.5	107.5, 104.6, 104.5, 101.8	39.56, 39.25, 38.83, 38.67	
$Mo(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**6**)	128.7, 120.5(C≡C)	207.4, 203.4	169.0	107.2, 104.7, 104.4, 101.3	12.77, 12.49, 12.29, 12.20	44.19, 43.91, 43.62
$W(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**7**)	140.6, 130.8(C≡C)	209.2 205.6	168.5	104.8, 100.2, 99.6, 97.9	39.30, 39.10, 38.82, 38.60	
$W(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**8**)	139.3, 130.0(C≡C)	207.7, 203.6		103.7, 100.8, 98.0	12.73, 12.23, 12.09, 11.50	44.50, 44.09 43.86, 43.68

[a] Measured in $CDCl_3$ containing Me_4Si as internal reference; amount of **1** insufficient for measurement. [b] CH_2 groups of $(C_8H_{12})_2CO$ and C_8H_{12} gave numerous peaks in the region δ 22–34 ppm. [c] Not observed.

through the cyclopentadienone ligand. As noted elsewhere [5], the ^{13}C chemical shifts in cyclopentadienone complexes are all deshielded with respect to those in uncoordinated $\alpha\beta$-unsaturated ketones, probably as a consequence of withdrawal of π-electron density into the metal *d*-orbitals. The two higher field peaks are assigned to the outer diene carbon atoms, i.e. those next to the C=O group, the two at lower field are assigned to the inner diene carbon atoms [4,5].

The $^{13}C\{^1H\}$ NMR spectra of **5**–**8** contain two signals at δ ca. 125–140 ppm due to the coordinated carbon atoms of cyclooctyne, these being inequivalent on the NMR time scale at room temperature. Their chemical shifts are in the region characteristic of 2π-electron donation [6] and are ca. 10 ppm more shielded for the tungsten complexes than for the corresponding molybdenum compounds. This correlates with the trend in ν(C≡C) mentioned above and probably has a similar origin. The ^{13}C≡O resonances of the tungsten complexes **3** and **4** were located in the usual region of δ ca. 220 ppm.

The ^{1}H NMR spectra due to the R_2NCS_2 groups (Table 1) confirm the conclusions based on $^{13}C\{^1H\}$ NMR spectra. In the case of $Mo(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**1**) and $Mo(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**5**), four singlets due to the inequivalent methyl groups are observed, while for the corresponding tungsten compounds **3** and **7** two of the lines overlap. The methyl and methylene resonances for the corresponding Et_2NCS_2 compounds appear as overlapping multiplets in the regions δ 1.0–1.5 ppm and 3–4 ppm respectively. All the complexes show in their ^{1}H NMR spectra broad, poorly resolved absorption in the region δ 0.9–3.0 ppm due to the CH_2 protons of the eight-membered rings.

The spectroscopic data for **1**–**8** suggest that the complexes are seven-coordinate, the metal atom being coordinated by two dtc ligands in inequivalent environments, a *tetrahapto*-bis(hexamethylene)cyclopentadienone and either CO (**1**–**4**) or cyclooctyne (**5**–**8**). To confirm this conclusion and to establish the detailed coordination geometry about the metal atom, a single crystal X-ray structural analysis of **3** has been carried out.

Structure of $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ *(3)*

The crystal structure analysis of **3** confirms the conclusion given above and provides the first structural characterization of a cyclopentadienone complex of a third row element. The stereochemical arrangement is shown, together with the atom labelling scheme, in Fig. 1 and, somewhat more clearly, by the stereopair in Fig. 2. The coordination geometry is best visualized as a distorted pentagonal bipyramid (II), with the CO ligand [C(18)–O(2)] and one of the sulphur atoms [S(3)] of a bidentate Me_2NCS_2 ligand in the axial positions; the equatorial sites are occupied by the other sulphur atom, S(4), of this dtc ligand, the sulphur atoms S(1) and S(2) of the second bidentate dtc ligand, and the mid-points CG(1) and CG(2) of the C=C bonds C(1)–C(8) and C(10)–C(17), respectively, of *tetrahapto*-bis(hexamethylene)cyclopentadienone. Despite substantial angular deformations due to the small bite-angles of the three chelating ligands, geometric parameters calculated with normalized metal–ligand (4S, 1CO, 2CG) distances are thoroughly characteristic of the 1/5/1 pentagonal bipyramidal arrangement [7] (Table 3). In contrast, the closely related complexes $W(S_2CNMe_2)_2(CO)_3$ [8] and $W(S_2CNEt_2)_2(CO)_2(PPh_3)$ [9] each exhibit 4/3 coordination about the metal atom.

The metal–sulphur distances in **3** [2.484(1)–2.547(1) Å] are slightly but signifi-

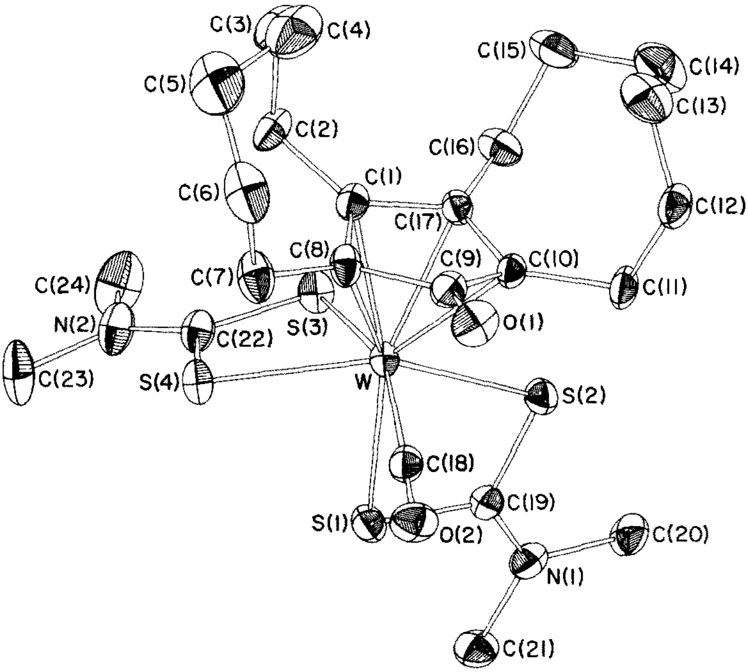


Fig. 1. Molecular structure and atom numbering of $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (3). Hydrogen atoms have been omitted for clarity; their numbering corresponds to that of the attached carbon atoms.

cantly shorter than those in $W(S_2CNMe_2)_2(CO)_3$ [2.501(2)–2.569(3) Å] [8] and in $W(S_2CNEt_2)_2(CO)_2(PPh_3)$ [2.487(3)–2.562(3) Å] [9], possibly owing to the extensive withdrawal of electron density from the metal atom by the cyclopentadienone ligand, leading to better σ-bonding by the sulphur atoms. Surprisingly, three of the

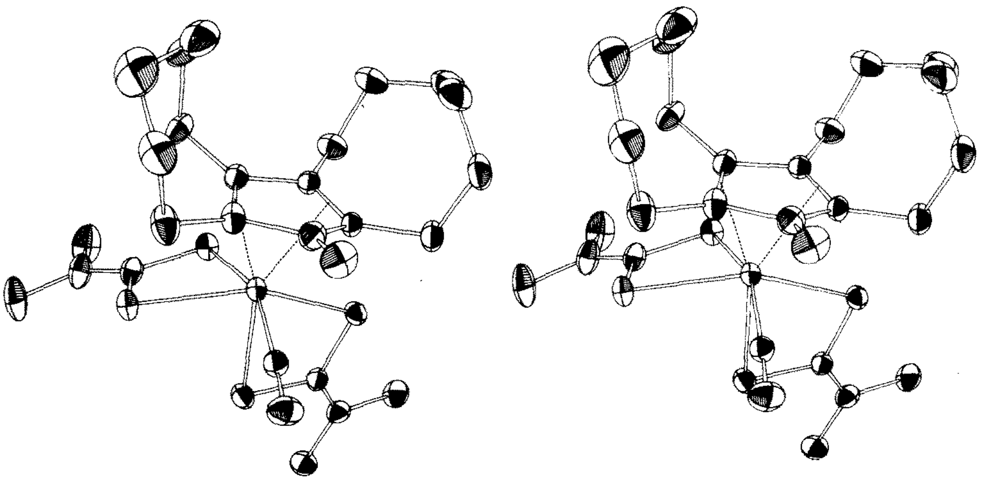
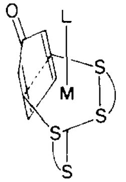


Fig. 2. Stereopair of the molecular structure of $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (3). Comments for Fig. 1 refer here also.



II

S—S = Me_2NCS_2, Et_2NCS_2
L = CO or cyclooctyne
M = Mo, W
hexamethylene groups on the coordinated cyclopentadienone have been omitted for clarity

four M–S distances in the formally octahedral acetylene complex W$(S_2CNEt_2)_2(CO)(C_2H_2)$ [2.550(1)–2.588(2) Å] [10] are either at the upper end of the range or exceed those observed for **3**, whereas the remaining distance [2.399(3) Å] is significantly shorter than the smallest value observed in **3** [2.484(1) Å]. The M–C(carbonyl) distance in $W(S_2CNEt_2)_2(CO)(C_2H_2)$ [1.936(7) Å] is also significantly shorter than that in **3** [1.980(4) Å], apparently indicative of stronger M–CO back-bonding in the former compound, although this feature is not reflected in the ν(CO) values [1921 cm^{-1} (Nujol) for **3**, 1960 cm^{-1} (KBr) [10] or 1925 cm^{-1} (toluene) for the C_2H_2 complex [11]].

As expected, both the C(8), C(9), O(1), C(10) (ketone) and C(8), C(1), C(17), C(10) (conjugated diene) groups are planar, within experimental error, the interplane dihedral angle of 17.6° being at the upper end of the range observed for various substituted cyclopentadienone complexes of $Fe(CO)_3$ and $Co(\eta\text{-}C_5H_5)$ (Table 4). The C–C distances in the diene fragment are almost equal to each other and to those found in the iron and cobalt complexes (Table 4). Moreover, the metal–carbon bond lengths to the central carbon atoms of the η^4-diene moiety [2.266(4), 2.261(4) Å] are shorter than those to the outer carbon atoms [2.385(3), 2.371(4) Å], a feature that is characteristic of 1,3-diene complexes in general [19] and of the cyclopentadienone

TABLE 3

COMPARISON OF OBSERVED AND IDEAL PENTAGONAL BIPYRAMID PARAMETERS (°) [a,b,c]

Parameter		Observed	Ideal
δ'		40–74	54.4
L_{eq}–M–L_{eq}		50–85	72
L_{ax}–M–L_{ax}		155	180
L_{eq} angular devn. from best plane	max	7.4	0
	mean	4.6	0

[a] L_{eq} sites defined by S(1), S(2), S(4) and the olefin [C(1)–C(8), C(10)–C(17)] mid-points. [b] δ' values are dihedral angles between adjoining triangular faces: δ' and L_{eq} angular deviations both calculated for normalised (unit bond length) coordinates. [c] Ideal values from ref. 7.

complexes listed in Table 4 in particular. These observations suggest that the formalism used to describe the metal–diene bonding in the latter [13,19,20] are equally applicable to **3**.

The dimensions of the dithiocarbamate ligands in **3** agree closely with those in $W(S_2CNMe_2)_2(CO)_3$ [8]. The C–C single bond distances in the eight-membered rings are unexceptional (av. 1.527 Å, sp^3–sp^3; 1.495 Å, sp^3–sp^2). However, internal ring angles are consistently larger (av. 6.2°) than values for unstrained rings, the r.m.s. deviations being similar for both rings (6.0, 6.2°). The rings have different configurations, but both can be described as skew-boat.

Complexes **5**–**8** are presumably isostructural with **3**, CO being replaced by η^2-cyclooctyne.

Discussion

It has been known for many years that acetylenes react with metal carbonyls on heating to give cyclopentadienone complexes, among many other products [21–23]. However, this type of condensation has not been reported hitherto in the reaction of acyclic alkynes with the dialkyldithiocarbamato carbonyl complexes of molybdenum and tungsten. In the case of molybdenum, the first formed product, $Mo(S_2CNR_2)_2$-(CO)(alkyne) loses CO on heating with an excess of aryl- or alkyl-substituted alkyne to give bis(alkyne) complexes $Mo(S_2CNR_2)_2(alkyne)_2$, the reaction being most rapid with the highly electrophilic alkyne $MeO_2CC_2CO_2Me$ [24]. Thus the formation of molybdenum and tungsten dialkyldithiocarbamato complexes containing I provides yet another indication of the high reactivity of cyclooctyne towards transition metal-containing compounds. This was already evident from the reports that cyclooctyne reacts even at room temperature with $Ni(CO)_4$ and with $Fe(CO)_5$ to give complexes of I, $Ni\{(C_8H_{12})_2CO\}_2$ and $Fe(CO)_3\{(C_8H_{12})_2CO\}$, respectively [25,26].

The fact that the relative proportions of **1**–**4** and **5**–**8** are sensitive to reaction conditions even though these products, once formed, cannot be readily interconverted suggests that there is a labile intermediate for which cyclooctyne and CO compete. Little is known about the mechanism of formation of cyclopentadienones from metal carbonyls and acetylenes, and it is not even certain, in most cases, whether the fragments are assembled in a mononuclear or polynuclear complex. In the present case, the former seems more likely. Following Pino and Braca [22], we suggest that the first-formed cyclooctyne complex $M(S_2CNR_2)_2(CO)(C_8H_{12})$ is transformed, under the influence of an excess of cyclooctyne, into a metallacyclobutenone (III) (Scheme 1). Cyclooctyne can then insert at either of the metal–carbon σ-bonds to give isomeric metallodienone complexes IV or V. Reductive coupling of the metal–carbon σ-bonds in both species would give the 16e fragment $M(S_2CNR_2)_2$(cyclopentadienone) (VI), which could rapidly pick up either CO or cyclooctyne to give the observed products.

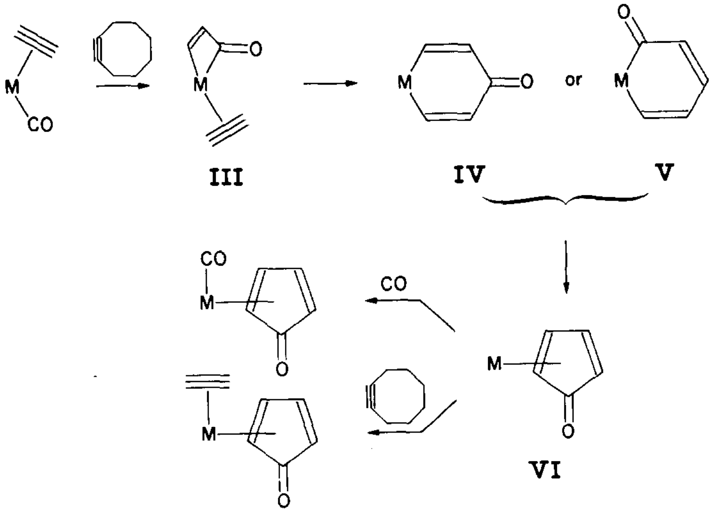
Although this proposal is speculative, there is precedent for some of the proposed intermediates. Metallocyclobutenones have been isolated from the reactions of hexafluorobut-2-yne with $Ru(CO)_3\{P(OMe)_3\}_2$ [27] and $Ir(\eta\text{-}C_5Me_5)(CO)_2$ [28]. No mononuclear metallocyclohexadienone is known, but the reaction between $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and hexafluorobut-2-yne gives a dinuclear complex VII in which a ferracyclohexadienone is attached through its double bonds to a second iron

TABLE 4

COMPARISON OF C–C BOND DISTANCES AND RING DIHEDRAL ANGLES IN CYCLOPENTADIENONE COMPLEXES

	Bond distances (Å) [a]					Dihedral angle (°)	Ref.
	C(9)–C(10)	C(10)–C(17)	C(17)–C(1)	C(1)–C(8)	C(8)–C(9)		
Co(η-C_5H_5)(C_4Me_4CO)	← 1.43(av.) →					9	12
Co(η-C_5H_5){$C_4(CF_3)_4CO$}	1.50(3)	1.49(3)	1.44(3)	1.40(3)	1.49(3)	21.3	13
$Fe(CO)_3${$C_4(CF_3)_4CO$}	1.46(4)	1.37(2)	1.40(2)	1.42(3)	1.50(3)	20.1	14
$Fe(CO)_3(C_4H_4CO)$	1.466(7)	1.416(9)	1.463(11)	1.416(9) [b]	1.466(7) [b]	19.9	15
$Fe(CO)_3${$C_4(C_2Me)_2Me_2CO$}	1.469(9)	1.412(8)	1.442(8)	1.435(8)	1.458(9)	14.1	16
Co(η-C_5H_5){$C_4(Ph)_2(mes)_2CO$} [c]	1.468(4)	1.445(4)	1.438(4)	1.436(4)	1.473(4)	10.9	17
{$Fe(CO)_3(C_4H_4CO)$}$_2$·1,4-$C_6H_4(OH)_2$	1.462(5)	1.394(5)	1.405(5)	1.402(5)	1.467(5)	16.1	18
$W(S_2CNMe_2)_2(CO)${$(C_8H_{12})_2CO$} (3)	1.478(6)	1.418(5)	1.460(5)	1.437(6)	1.467(6)	17.6	this work

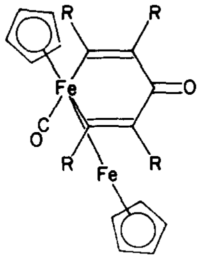
[a] Relative, not absolute, bond positions. [b] Equivalent by symmetry to a preceding distance. [c] mes = mesityl, 1,3,5-$C_6H_2Me_3$.



SCHEME 1. M = $Mo(S_2CNMe_2)_2$, $Mo(S_2CNEt_2)_2$, $W(S_2CNMe_2)_2$ or $W(S_2CNEt_2)_2$; hexamethylene groups have been omitted for clarity.

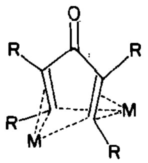
atom [29], and complexes containing a pentadienone unit bound to two metal atoms as in VIII have been isolated from the reactions of iron carbonyls and of Rh(η-C_5H_5)$(CO)_2$ with various acetylenes [30–32].

The ease with which cyclooctyne forms the bis(hexamethylene)cyclopentadienone



VII

R = CF_3



VIII

R = various alkyl or aryl substituents
M = $Fe(CO)_3$ or Rh(η-C_5H_5)

TABLE 5

ANALYTICAL DATA FOR BIS(HEXAMETHYLENE)CYCLOPENTADIENONE COMPLEXES OF MOLYBDENUM AND TUNGSTEN [a]

	M.p. (°C)	Analysis (Found (calcd.)(%))		
		C	H	N
$Mo(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ **(1)**	166(dec.)	47.4 (47.35)	6.1 (6.0)	4.8 (4.6)
$W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ **(3)**	ca. 200(dec.)	41.2 (41.4)	5.2 (5.2)	4.0 (4.0)
$W(S_2CNEt_2)_2(CO)\{(C_8H_{12})_2CO\}$ **(4)**	ca. 175(dec.)	44.1 (44.7)	5.9 (5.9)	3.5 (3.7) [b]
$Mo(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ **(5)**	138	54.0 (54.05)	7.5 (7.0)	3.5 (4.1) [c]
$Mo(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ **(6)**	114(dec.)	57.6 (56.4)	7.9 (7.6)	3.8 (3.8)
$W(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ **(7)**	212	47.6 (47.9)	6.2 (6.2)	3.4 (3.6)
$W(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ **(8)**	110(dec.)	49.7 (50.5)	6.9 (6.8)	3.3 (3.4) [d]

[a] Analyses for S were generally 5–20% below calcd. values. [b] %S: found, 16.6; calcd. 17.0. [c] %S: found, 16.8; calcd. 18.6. [d] %S: found, 13.2; calcd. 15.4.

complexes described here suggests that similar reactions would probably occur with the short-lived smaller ring alkynes cycloheptyne and cyclohexyne. Thus the dialkyldithiocarbamato carbonyl complexes of molybdenum and tungsten are unlikely to be suitable trapping agents for these very reactive molecules.

Experimental

The preparation of starting materials and the experimental and spectroscopic procedures used have been described [1]. The complexes $W(S_2CNR_2)_2(CO)_2(PPh_3)$ (R = Me, Et) were made from $W(S_2CNR_2)_2(CO)_3$ and triphenylphosphine [9]. Spectroscopic data are collected in Tables 1 (IR, ^1H NMR) and 2 (^{13}C), analytical data are in Table 5.

Preparations

Bis(dimethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}carbonylmolybdenum(II), $Mo(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ *(1).* Cyclooctyne (308 μl, 2.48 mmol) was added to a slurry of $Mo(S_2CNMe_2)_2(CO)_2(PPh_3)$ (0.72 g, 1.10 mmol) in THF (5 ml) and ether (20 ml) under CO. The resulting brown solution was stirred for 30 min and cooled to −20°C overnight. The brown solid that separated contained approximately equal amounts of **1** and $Mo(S_2CNMe_2)_2(C_8H_{12})$-$\{(C_8H_{12})_2CO\}$ (**5**), as judged by the relative intensities of the $\nu(C\equiv O)$ and $\nu(C=O)$ IR bands. Recrystallization from acetonitrile/methanol gave 80 mg (12%) of orange, crystalline **1**.

Bis(dimethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}(cyclooctyne)-molybdenum(II), $Mo(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (5). Cyclooctyne (314 μl, 2.52 mmol) was added to a slurry of $Mo(S_2CNMe_2)_2(CO)_2(PPh_3)$ (0.55 g, 0.84 mmol) in THF (5 ml) and ether (20 ml). The slurry turned green then orange over a period of ca. 15 min. The mixture was stirred for a further hour, then cooled to −20°C overnight. The orange solid was filtered off, washed with ether and dried. It was shown by IR spectroscopy to contain **1** and **5**. Recrystallization from THF gave **5** as orange microcrystals (0.30 g, 49%).

Bis(diethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}(cyclooctyne)-molybdenum(II), $Mo(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (6). This was prepared similarly to **5** from cyclooctyne (368 μl, 2.96 mmol) and $Mo(S_2CNEt_2)_2(CO)_2(PPh_3)$ (0.70 g, 0.99 mmol). The yellow solid that separated overnight at −20°C was an approximately 4/1 mixture of **6** and $Mo(S_2CNEt_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**2**), as shown by IR spectroscopy. Recrystallization from acetonitrile/methanol gave yellow microcrystals of **6** (0.3 g, 39%). **2** could not be separated from **6**.

Bis(dimethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}carbonyl-tungsten(II), $W(S_2CNMe_2)_2(CO)\{C_8H_{12})_2CO\}$ (3). Cyclooctyne (254 μl, 2.04 mmol) was added to a slurry of $W(CO)_3(S_2CNMe_2)_2$ (0.46 g, 0.91 mmol) in THF (5 ml) and ether (20 ml) The slurry turned green then orange over a period of less than 1 min. The mixture was stirred for 30 min and cooled to −20°C overnight. The

TABLE 6

DETAILS OF X-RAY DATA COLLECTION FOR $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (3)

Radiation	Mo-$K_{\bar{\alpha}}$ (0.7107 Å)
Monochromator	graphite
Scan technique	θ–2θ
Scan speed	2° min^{-1} 2θ
Limits of collection	$4 < 2\theta < 60°$
Bkgd counting time [a]	2×10 s
Std reflections [b]	12 0 0 0 12 0 0 0 8
Forms recorded	$\pm h\ k\ l$
Total reflections measd	8526
No. of unique "obsd" reflections [c]	5811
Crystal stability [d]	3% isotropic decay
R_s [e]	0.02
R_{int} [f]	0.02
Crystal dimensions	0.016×0.011×0.032 cm (parallel to 110, $\bar{1}$10, 001 reciprocal lattice vectors respectively)
μ(Mo-$K_{\bar{\alpha}}$)	44.11 cm^{-1}
Absorption correction	numerical (SHELX)
Transmission coeff. range	0.51(min) 0.65(max)
Temp. during collection	21 ± 1°C

[a] Backgrounds counted for 10 s at each scan extremity; stationary crystal-stationary counter. [b] Monitored every 100 min. [c] Having $I \geqq 3\sigma(I)$. [d] Data corrected accordingly. [e] R_s (the statistical R factor) = $\Sigma\sigma_s(F_0)/\Sigma|F_0|$. [f] $R_{int} = \{\Sigma(N\Sigma^N w(F_0 - \langle F_0\rangle)^2)/\Sigma((N-1)\Sigma^N wF_0^2)\}^{1/2}$ (SHELX).

resulting orange solid was filtered off, washed with ether, and dried in vacuo; IR spectroscopy showed it to be an approximately 2/1 mixture of **3** and **7**. Recrystallization from methanol/THF gave **3** as orange microcrystals (0.25 g, 40%).

Bis(dimethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}(cyclooctyne)-tungsten(II), $W(S_2CNMe_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ *(**7**).* Addition of cyclooctyne (182 μl, 1.46 mmol) to a solution of $W(S_2CNMe_2)_2(CO)(C_8H_{12})$ (0.41 g, 0.73 mmol) in THF (20 ml) caused the colour to change from green to orange over a period of a few min. The mixture was stirred for 30 min and evaporated to ca. 2 ml volume. Addition of ether (20 ml) precipitated a yellow solid which was set aside overnight at −20°C. IR spectroscopy showed it to be an approximately 4/1 mixture of **7** and **3**. Recrystallization from THF gave **7** as yellow microcrystals (0.19 g, 34%).

*Bis(diethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}carbonyltungsten(II) (**4**).* Addition of exactly 2 mol equiv. of cyclooctyne to $W(S_2CNEt_2)_2(CO)_2(PPh_3)$, as for **3**, generally gave an inseparable mixture of **4** and

TABLE 7

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**3**)

Atom	*x/a*	*y/b*	*z/c*
W	9156(0)	1729(0)	1917(0)
S(1)	8655(1)	576(1)	3305(1)
S(2)	10337(1)	618(1)	2343(1)
S(3)	8527(1)	649(1)	417(1)
S(4)	7518(1)	1848(1)	1667(1)
O(1)	10233(3)	3800(2)	2689(3)
O(2)	9287(3)	2648(2)	4365(3)
N(1)	9838(3)	−687(2)	3656(3)
N(2)	6741(3)	662(3)	261(4)
C(1)	9205(3)	2608(2)	344(4)
C(2)	8614(3)	2611(3)	−754(4)
C(3)	8892(5)	3285(4)	−1642(5)
C(4)	9166(5)	4135(4)	−1154(7)
C(5)	8451(6)	4597(5)	−546(9)
C(6)	8548(4)	4650(3)	832(7)
C(7)	8397(3)	3805(3)	1470(6)
C(8)	9124(3)	3177(2)	1323(5)
C(9)	9990(3)	3263(3)	1970(4)
C(10)	10474(2)	2503(3)	1592(4)
C(11)	11402(3)	2331(3)	2050(5)
C(12)	12051(3)	2966(4)	1507(6)
C(13)	11964(4)	3042(4)	165(7)
C(14)	12018(4)	2239(6)	−496(7)
C(15)	11111(4)	1947(5)	−1129(5)
C(16)	10452(4)	1576(3)	−330(5)
C(17)	10060(3)	2181(2)	528(4)
C(18)	9258(3)	2306(3)	3471(4)
C(19)	9647(3)	65(3)	3177(4)
C(20)	10697(4)	−1096(3)	3470(5)
C(21)	9200(3)	−1144(3)	4334(5)
C(22)	7501(3)	1018(3)	689(4)
C(23)	5877(3)	950(5)	619(7)
C(24)	6743(4)	−53(4)	−577(7)

$W(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ (**8**). On one occasion **4** was isolated in a pure state from this reaction in 20% yield, but the conditions have not yet been reproduced.

Bis(diethyldithiocarbamato){bis(hexamethylene)cyclopentadienone}(cyclooctyne)-tungsten(II), $W(S_2CNEt_2)_2(C_8H_{12})\{(C_8H_{12})_2CO\}$ *(8).* Cyclooctyne (374 μl, 3.00 mmol) was added to a solution of $W(CO)_3(S_2CNEt_2)_2$ (0.60 g, 1.07 mmol) in THF (30 ml). The colour changed very rapidly through green to orange-brown. The solution was evaporated to dryness under reduced pressure. The residue was triturated with pentane, dried in vacuo, and recrystallized from acetonitrile to give yellow microcrystals of **8** (0.16 g, 20%).

Collection and reduction of X-ray intensity data

Single crystals of $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (**3**) were grown by allowing ether to diffuse slowly into a saturated solution of the complex in dichloromethane.

Crystal data. $C_{24}H_{36}N_2O_2S_4W$, FW 696.7, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$), a 15.132(1), b 15.705(2), c 11.346(1) Å, β 93.68(2)°, V_c 2690.8 Å^3, ρ_{obsd} 1.72(1), ρ_{calcd} 1.720 g cm^{-3}, $Z = 4$, $F(000) = 1392$, μ(Mo-K_α) 44.11 cm^{-1}; T 21 ± 1°C.

Reflection intensities were measured on a Philips PW1100/20 diffractometer and were reduced to $|F_0|$ and $\sigma(F_0)$ values as described previously ($p^2 = 0.008$ assumed) [33,34]. Details are summarized in Table 6. Quoted cell dimensions and e.s.d.'s derive from least-squares analysis [35] of the setting angles 2θ, ω, χ, and ϕ,

TABLE 8

BOND DISTANCES (Å) AND ESTIMATED STANDARD ERRORS FOR $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (3)

W–S(1)	2.547(1)	C(7)–C(8)	1.495(6)
W–S(2)	2.522(1)	C(8)–C(1)	1.437(6)
W–S(3)	2.544(1)	C(8)–C(9)	1.467(6)
W–S(4)	2.484(1)	C(9)–O(1)	1.214(5)
W–C(1)	2.261(4)	C(9)–C(10)	1.478(6)
W–C(8)	2.371(4)	C(10)–C(11)	1.489(5)
W–CG(1) [a]	2.203(4)	C(11)–C(12)	1.554(6)
W–C(10)	2.385(3)	C(12)–C(13)	1.525(9)
W–C(17)	2.266(4)	C(13)–C(14)	1.472(9)
W–CG(2) [a]	2.216(4)	C(14)–C(15)	1.576(8)
W–C(18)	1.980(4)	C(15)–C(16)	1.507(6)
S(1)–C(19)	1.718(4)	C(16)–C(17)	1.510(6)
S(2)–C(19)	1.693(4)	C(17)–C(1)	1.460(5)
S(3)–C(22)	1.705(4)	C(17)–C(10)	1.418(5)
S(4)–C(22)	1.712(4)	C(18)–O(2)	1.146(5)
C(1)–C(2)	1.487(5)	C(19)–N(1)	1.326(5)
C(2)–C(3)	1.539(7)	C(20)–N(1)	1.477(6)
C(3)–C(4)	1.494(8)	C(21)–N(1)	1.461(5)
C(4)–C(5)	1.506(9)	C(22)–N(2)	1.340(5)
C(5)–C(6)	1.564(10)	C(23)–N(2)	1.465(6)
C(6)–C(7)	1.535(7)	C(24)–N(2)	1.474(7)

[a] CG(1), CG(2) are C(1)–C(8) and C(10)–C(17) mid-points, respectively.

determined for 12 carefully centred reflections ($23.5 < 2\theta < 36.8°$; $\lambda = 0.70926$ Å) on a Picker FACS-1 diffractometer.

Solution and refinement of the structure. The structure was solved from conventional Patterson and Fourier syntheses and refined by full matrix least-squares with SHELX [36]. Anisotropic thermal parameters were specified for all non-hydrogen atoms. The twenty-four methylene hydrogen atoms (located by calculation; C–H 0.95 Å assumed) of the cyclopentadienone ligand were included in the scattering model with a single (refined) isotropic thermal parameter. The methyl hydrogen atoms of the dimethyldithiocarbamate ligands could not be located and were not included. The function minimized was $\Sigma w \| F_0 | - G | F_c \|^2$ with $w = \sigma(F_0)^{-2}$. Scattering factors, together with anomalous dispersion corrections, were taken from Ref. 37. Data showed no evidence of extinction effects and no correction was applied. At convergence $R = 0.027$ and $R_w = 0.045$ [38] for 5811 [$I \geq 3\sigma(I)$] unique data. Shift/e.s.d. ratios were uniformly less than 0.35 and electron density excursions in a terminal difference Fourier synthesis did not exceed ±1 eÅ^{-3}. Terminal non-hydrogen atom coordinates are listed in Table 7 and corresponding bond lengths and bond angles in Tables 8 and 9. Tables of anisotropic thermal parameters, hydrogen atom coordinates (not refined), and observed and calculated structure

TABLE 9

SELECTED BOND ANGLES (deg) AND ESTIMATED STANDARD ERRORS FOR $W(S_2CNMe_2)_2(CO)\{(C_8H_{12})_2CO\}$ (3)

S(2)–W–S(1)	68.0(1)	C(9)–C(8)–C(1)	109.1(3)
S(2)–W–CG(2)	80.6(1)	C(7)–C(8)–C(1)	126.6(4)
CG(2)–W–CG(1)	50.4(2)	C(10)–C(9)–C(8)	103.0(3)
CG(1)–W–S(4)	85.1(1)	C(10)–C(9)–O(1)	128.5(4)
S(4)–W–S(1)	77.9(1)	C(8)–C(9)–O(1)	128.5(4)
S(3)–W–S(1)	80.0(1)	C(17)–C(10)–C(11)	126.0(4)
S(3)–W–S(2)	84.1(1)	C(17)–C(10)–C(9)	109.5(3)
S(3)–W–CG(2)	105.0(1)	C(11)–C(10)–C(9)	121.2(4)
S(3)–W–CG(1)	101.3(1)	C(12)–C(11)–C(10)	110.6(3)
S(3)–W–S(4)	69.3(1)	C(13)–C(12)–C(11)	115.4(4)
C(18)–W–S(3)	154.9(1)	C(14)–C(13)–C(12)	116.1(5)
C(18)–W–S(1)	77.6(1)	C(15)–C(14)–C(13)	114.0(5)
C(18)–W–S(2)	97.6(1)	C(16)–C(15)–C(14)	115.4(5)
C(18)–W–CG(2)	100.0(2)	C(17)–C(16)–C(15)	116.6(4)
C(18)–W–CG(1)	96.5(2)	C(16)–C(17)–C(10)	127.1(4)
C(18)–W–S(4)	95.0(1)	C(16)–C(17)–C(1)	125.3(4)
W–S(1)–C(19)	89.1(1)	C(10)–C(17)–C(1)	107.4(3)
W–S(2)–C(19)	90.4(1)	W–C(18)–O(2)	177.6(3)
W–S(3)–C(22)	87.6(1)	S(2)–C(19)–S(1)	112.4(2)
W–S(4)–C(22)	89.4(1)	S(2)–C(19)–N(1)	124.1(3)
C(8)–C(1)–C(2)	124.8(4)	S(1)–C(19)–N(1)	123.5(3)
C(17)–C(1)–C(2)	126.9(4)	S(4)–C(22)–S(3)	113.6(2)
C(17)–C(1)–C(8)	107.0(3)	S(4)–C(22)–N(2)	121.9(3)
C(3)–C(2)–C(1)	112.1(4)	S(3)–C(22)–N(2)	124.2(3)
C(4)–C(3)–C(2)	116.9(5)	C(21)–N(1)–C(20)	118.6(4)
C(5)–C(4)–C(3)	114.1(6)	C(21)–N(1)–C(19)	121.3(4)
C(6)–C(5)–C(4)	117.4(6)	C(20)–N(1)–C(19)	120.0(4)
C(7)–C(6)–C(5)	114.7(5)	C(24)–N(2)–C(23)	116.9(4)
C(8)–C(7)–C(6)	112.7(4)	C(24)–N(2)–C(22)	121.0(4)
C(9)–C(8)–C(7)	121.5(4)	C(23)–N(2)–C(22)	122.1(4)

factor amplitudes are available from the authors. Computational details are given in Ref. 39.

References

1 M.A. Bennett and I.W. Boyd, J. Organomet. Chem., 290 (1985) 165.

2 G.L. Hillhouse and B.L. Haymore, J. Am. Chem. Soc., 104 (1982) 1537.

3 P.S. Braterman, J.L. Davidson and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1976) 421; J.L. Davidson, M. Green, F.G.A. Stone and A.J. Welch, ibid., 738.

4 L. Kruczynski and J. Takats, Inorg. Chem., 15 (1976) 3140.

5 R.S. Dickson and S.H. Johnson, Aust. J. Chem., 29 (1976) 2189.

6 J.L. Templeton and B.C. Ward, J. Am. Chem. Soc., 102 (1980) 3288.

7 M.G.B. Drew, Prog. Inorg. Chem., 23 (1977) 67.

8 J.L. Templeton and B.C. Ward, Inorg. Chem., 19 (1980) 1753.

9 J.L. Templeton and B.C. Ward, J. Am. Chem. Soc., 103 (1981) 3743.

10 L. Ricard, R. Weiss, W.E. Newton, G.-J.J. Chen and J.W. McDonald, J. Am. Chem. Soc., 100 (1978) 1318.

11 B.C. Ward and J.L. Templeton, J. Am. Chem. Soc., 102 (1980) 1532.

12 L.F. Dahl and D.L. Smith, J. Am. Chem. Soc., 83 (1961) 752.

13 M. Gerloch and R. Mason, Proc. Roy. Soc., A279 (1964) 91.

14 N.A. Bailey and R. Mason, Acta Cryst., 21 (1966) 652.

15 K. Hoffmann and E. Weiss, J. Organomet. Chem., 128 (1977) 237.

16 G.G. Cash and R.C. Petterson, Inorg. Chem., 17 (1978) 650.

17 A. Clearfield, P. Rudolf, I. Bernal and M.D. Rausch, Inorg. Chim. Acta, 42 (1980) 17.

18 K.-J. Jens and E. Weiss, J. Organomet. Chem., 210 (1980) C27.

19 See, e.g. C. Krüger, B.L. Barnett and D. Brauer in E.A. Koerner von Gustorf, F.-W. Grevels and I. Fischler (Eds.), The Organic Chemistry of Iron, Vol. 1, Academic Press, New York, 1978, p. 1, and references cited therein.

20 R. Mason and M.R. Churchill, Adv. Organomet. Chem., 5 (1967) 93.

21 W. Hübel in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 1, Wiley-Interscience, 1968, p. 273.

22 P. Pino and G. Braca, Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley-Interscience, 1977, p. 419.

23 R.S. Dickson and P.J. Fraser, Adv. Organomet. Chem., 12 (1974) 323.

24 R.S. Herrick and J.L. Templeton, Organometallics, 1 (1982) 842.

25 G. Wittig and P. Fritze, Annalen, 712 (1968) 79.

26 H. Kolshorn, H. Meier and E. Müller, Tetrahedron Lett., (1971) 1469.

27 R. Burt, M. Cooke and M. Green, J. Chem. Soc. A, (1970) 2981.

28 P.A. Corrigan, R.S. Dickson, G.D. Fallon, L.J. Michel and C. Mok, Aust. J. Chem., 31 (1978) 1937.

29 J.L. Davidson, M. Green, F.G.A. Stone and A.J. Welch, J. Chem. Soc., Chem. Commun., (1975) 286.

30 J. Piron, P. Piret, J. Meunier-Piret and M. Van Meerssche, Bull. Soc. Chim. Belg., 78 (1969) 121.

31 F.A. Cotton, D.L. Hunter and J.M. Troup, Inorg. Chem., 15 (1976) 63.

32 R.S. Dickson, B.M. Gatehouse and S.H. Johnson, Acta Cryst., B33 (1977) 319; P.A. Corrigan and R.S. Dickson, Aust. J. Chem., 34 (1981) 1401; P.A. Corrigan, R.S. Dickson, S.H. Johnson, G.N. Pain and M. Yeoh, ibid., 35 (1982) 2203.

33 G.B. Robertson and P.O. Whimp, J. Am. Chem. Soc., 97 (1975) 1051.

34 W.R. Busing and H.A. Levy, J. Chem. Phys., 26 (1957) 563; P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 197.

35 W.R. Busing and H.A. Levy, Acta Cryst., 22 (1967) 457.

36 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge University, England.

37 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV, pp. 99, 149.

38 $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$.

39 Computations were carried out with both ANUCRYS [40] and SHELX [36] programs on the ANU Computer Services Centre's UNIVAC 1100/82 computer. The molecular diagrams were drawn with ORTEP [41].

40 G.M. McLaughlin, D. Taylor and P.O. Whimp, The ANUCRYS Structure Determination Package, Research School of Chemistry, ANU, Canberra.

41 C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee.