Journal of Organometallic Chemistry, 290 (1985) 165–180
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MONO-CYCLOOCTYNE COMPLEXES OF DIVALENT AND TETRAVALENT MOLYBDENUM AND TUNGSTEN

MARTIN A. BENNETT* and IAN W. BOYD

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601 (Australia)

(Received January 30th, 1985)

Summary

Cyclooctyne (C_8H_{12}) reacts with the dialkyldithiocarbamato complexes $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ and $W(S_2CNR_2)_2(CO)_3$ (R = Me, Et) in a 1 : 1 mol ratio to give the divalent metal alkyne complexes $M(S_2CNR_2)_2(CO)(C_8H_{12})$. These are oxidized by bromine or iodine to tetravalent metal alkyne complexes $MX_2(S_2CNR_2)_2(C_8H_{12})$ (M = Mo, W; X = Cl, Br; R = Me, Et). Carbon-13 NMR and IR spectroscopic data indicate that in these compounds and in the triethylphosphine complexes $MBr_2(CO)(C_8H_{12})(PEt_3)_2$ (M = Mo, W) cyclooctyne behaves as a 4π-electron donor, whereas in the oxomolybdenum(IV) cyclooctyne complexes $MoO(S_2CNR_2)_2C_8H_{12})$ (R = Me, Et) it donates approximately 3π-electrons owing to competing π-donation from the oxo ligand.

Introduction

The simplest unsubstituted cyclic alkyne that can be isolated in the free state is the eight-membered ring cyclooctyne (C_8H_{12}), and this is much more reactive than its acyclic counterparts towards Diels–Alder reagents and transition metal compounds [1,2]. It readily forms mononuclear complexes with Cu^I [3], Ag^I [3], Pt^0 [3–5] and Mo^0 [6] and is catalytically cyclotrimerized to tris(hexamethylene)benzene at room temperature by $NiBr_2$ [7], $Ni(CN)_2$ [6], $Ni(CH_2{=}CHCN)_2$ [3], $Pt(PPh_3)_2(C_8H_{12})$ [3], $TiCl_4$ [8], $Fe(CO)_5$ [9] and $Mo(CO)_6$ [6]. The reaction of $Co_2(CO)_8$ with cyclooctyne in a 1 : 1 mol ratio gives the expected μ-alkyne complex $Co_2(CO)_6(C_8H_{12})$, but, when an excess of cyclooctyne is used, a dinuclear cobaltacyclopentadiene complex $Co_2(CO)_5(C_8H_{12})_2$ is also formed, even at room temperature; both compounds catalyse the cyclotrimerization of cyclooctyne [10,11].

Recent work has shown that alkynes form stable complexes with both divalent and tetravalent molybdenum and tungsten, the auxiliary ligands generally being various combinations of halide, cyclopentadienyl, carbon monoxide, tertiary phosphines and anionic sulphur donor ligands. A particularly extensive range of alkyne

0022-328X/85/$03.30

complexes of molybdenum and tungsten containing dithiophosphinate (R_2PS_2) and dialkyldithiocarbamato (dtc, R_2NCS_2) ligands has been prepared and structurally characterized, mainly by McDonald and Templeton and their respective co-workers [12–20], and convincing evidence has been presented in support of the idea that, in these and other complexes, alkynes can donate between two and four electrons to the metal atom by means of their orthogonal pairs of π-orbitals [12–14,17,18–23]. We were interested to see whether dialkyldithiocarbamate complexes of molybdenum and tungsten could be used in the same way at $Pt(PPh_3)_3$ [5] to trap very reactive, short-lived small ring alkynes such as cycloheptyne and cyclohexyne that cannot be isolated in the free state [1,2]. For this purpose it was necessary first to examine the behaviour of cyclooctyne with these complexes and the results are reported in this and the following paper [24].

Results

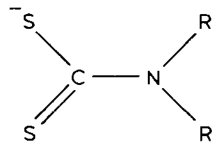
When one mol equiv. of cyclooctyne is added at room temperature to either $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ or $W(S_2CNR_2)_2(CO)_3$ (R = Me, Et) dissolved in THF, bright green solutions are formed. After addition of ethanol, bright green crystalline complexes of formula $M(S_2CNR_2)_2(CO)(C_8H_{12})$ (**1**–**4**) can be isolated in ca. 50% yield (eq. 1).

$$M(S_2CNR_2)_2(CO)_2L + C_8H_{12} \rightarrow M(S_2CNR_2)_2(CO)(C_8H_{12}) + CO + L \qquad (1)$$

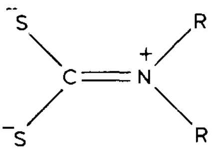
(L = PPh_3, M = Mo; (M = Mo; R = Me (**1**), Et (**2**);
L = CO, M = W) M = W, R = Me (**3**), Et (**4**))

These complexes can only be isolated if the mol ratio of reactants is close to 1 : 1, because they readily react with more cyclooctyne to give complexes containing bis(hexamethylene) cyclopentadienone [24]. In contrast, the corresponding, similarly prepared complexes of acyclic alkynes react only under forcing conditions with an excess of alkyne to give bis(alkyne) complexes $M(S_2CNR_2)_2(\text{alkyne})_2$ [21]. Because of this sensitivity to the mol ratio of reactants, we have used as the molybdenum-containing precursor $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ rather than the di- or tri-carbonyls $Mo(S_2CNR_2)_2(CO)_n$ (n = 2 or 3), which are difficult to obtain in a pure state (see Experimental).

The spectroscopic properties of **1**–**4** are similar to those of the corresponding acyclic alkyne complexes [13,14,17,19]. The IR spectra show one strong ν(CO) band in the region 1880–1920 cm^{-1} and a ν(C–N) band at ca. 1500 cm^{-1} (Table 1), but there was no absorption in the 1600–1900 cm^{-1} region assignable to ν(C≡C) modified by coordination. The ν(CO) values for the tungsten complexes are ca. 20 cm^{-1} lower than for the corresponding molybdenum compounds, reflecting the stronger bonding of CO to the third row element, and are consistently higher by a few cm^{-1} for Et_2NCS_2 than for Me_2NCS_2. Moreover, the ν(C⩦N) values for corresponding pairs are always in the order $Me_2NCS_2 > Et_2NCS_2$ and are always higher for tungsten than for molybdenum. Similar observations have been made for a series of diazoalkane complexes $W(CO)(N_2CR'_2)(S_2CNR_2)_2$ (R = Me, Et; R′ = various aryl groups) [25] and it has been suggested that Me_2NCS_2 donates more electron density to a metal than Et_2NCS_2because resonance form (**B**) is relatively more important than (**A**).

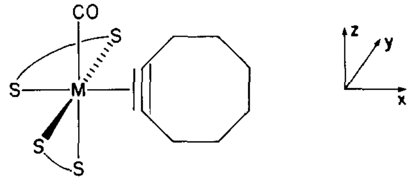


(A)



(B)

The ^1H NMR spectrum of **3** shows four singlets between δ 3.0 and δ 3.5 ppm due to the methyl protons of the dimethyldithiocarbamato ligands, showing that both the ligands themselves and the methyl groups on each ligand are inequivalent; in the case of **1**, the methyl resonances overlap to give a multiplet. The cyclooctyne methylene resonances appear as complex multiplets in the region δ 1–2 ppm. The conclusions drawn from the ^1H NMR spectra are confirmed by the $^{13}C\{^1H\}$ NMR spectra of **1–4** (Table 2), which show two signals of equal intensity at ca. δ 200 ppm arising from quaternary carbons of the inequivalent dtc ligands. The spectra of **2** and **4** show the expected four resonances for the methyl carbons of the Et_2NCS_2 groups but only three of the four methylene carbon resonances are observed, presumably owing to fortuitous overlap. Likewise, the $^{13}C\{^1H\}$NMR spectra of **1** and **3** show, respectively, only two and three of the expected four singlets due to the methyl carbons of the Me_2NCS_2 groups. At room temperature the $^{13}C\{^1H\}$ NMR spectra of **1–4** also contain singlets at ca. δ 240 ppm due to CO and at ca. δ 215–220 ppm due to the coordinated alkyne carbon atoms. The remarkable deshielding of the latter, which is also observed in the corresponding complexes of acyclic alkynes [17,19,21], is believed to indicate that the alkyne behaves as a 4π-electron donor. The spectroscopic data are therefore consistent with the pseudo-octahedral 18e structure I in which the coordinated triple bond is disposed parallel to the M–CO bond, as found in the acyclic alkyne complexes $Mo(S_2CNEt_2)_2(CO)(PhC_2Ph)$, $Mo(S_2CNEt_2)_2(CO)(PhC_2H)$ and $W(S_2CNEt_2)_2(CO)(HC_2H)$ [14]. This arrangement is that most suitable for four-electron donation from the alkyne, because it allows the filled alkyne $\pi_\perp$ orbital to overlap with the empty metal d_{xy} orbital while the filled $\pi_\parallel$ orbital overlaps with the empty metal $d_{x^2-y^2}sp^3$ hybrid orbital [14,19,22].



I

S—S = Me_2NCS_2, Et_2NCS_2
M = Mo, W

The cyclooctyne carbon atoms in structure I are inequivalent, and their NMR equivalence suggests that cyclooctyne is rotating rapidly about the metal–alkyne bond at room temperature. When solutions of **1–4** are cooled below room temperature, the alkyne carbon and α-CH_2 singlets at, respectively, δ 220 and 30 ppm each

(Continued on p. 171)

TABLE 1

^{1}H NMR AND SELECTED IR DATA FOR MOLYBDENUM AND TUNGSTEN CYCLOOCTYNE COMPLEXES

Complex		^{1}H NMR (δ (ppm)) [a]			IR (cm^{-1}) [b]
		CH_3(dtc/PEt_3)	CH_2(dtc/PEt_3)	CH_2(C_8H_{12})	
$Mo(S_2CNMe_2)_2(CO)(C_8H_{12})$	**(1)**	3.25m		3.7–3.1 br m, 2.1–1.5 br m	1896($C\equiv O$) [c], 1513($C\overset{\cdots}{-}N$)
$Mo(S_2CNEt_2)_2(CO)(C_8H_{12})$	**(2)**	1.25m	3.62m	3.9–3.5 br m, 2.0–1.0 br m	1900 ($C\equiv O$), 1489 ($C\overset{\cdots}{-}N$)
$W(S_2CNMe_2)_2(CO)(C_8H_{12})$	**(3)**	3.28s, 3.16_4s, 3.15_7s, 3.09s		3.51q, 1.85 br m, 1.5 br m	1878 ($C\equiv O$), 1525 ($C\overset{\cdots}{-}N$)
$W(S_2CNEt_2)_2(CO)(C_8H_{12})$	**(4)** [d]	1.43m	3.57m	3.9–3.4 br m, 2.0–1.0 br m	1881 ($C\equiv O$), 1492, 1501 ($C\overset{\cdots}{-}N$)
$MoBr_2(S_2CNMe_2)_2(C_8H_{12})$	**(5)**	3.37m		3.2–3.0m, 1.93 m, 1.55 m	1734 ($C\equiv C$), 1537 ($C\overset{\cdots}{-}N$)
$MoBr_2(S_2CNEt_2)_2(C_8H_{12})$	**(6)**	1.36m	3.8–3.3m, 2.0–1.2m		1751 ($C\equiv C$), 1510 ($C\overset{\cdots}{-}N$)
$WBr_2(S_2CNMe_2)_2(C_8H_{12})$	**(7)**	3.21m		3.5–3.2 m, 2.0–1.5 br m	1730 ($C\equiv C$), 1545 ($C\overset{\cdots}{-}N$)

$WBr_2(S_2CNEt_2)_2(C_8H_{12})$	**(8)**	ca. 1.4m	4.0–3.2m, 2.0–1.1 br m		1739 ($C\equiv C$), 1514 ($C\overset{...}{-}N$)
$MoI_2(S_2CNMe_2)_2)(C_8H_{12})$	**(9)**	3.4m		3.6–2.9m, 2.0–1.4m	1735 ($C\equiv C$), 1538 ($C\overset{...}{-}N$)
$MoI_2(S_2CNEt_2)_2(C_8H_{12})$	**(10)**	1.25m	4.0–3.4m, 2.0–1.0m		1510–1500 br ($C\overset{...}{-}N$)
$WI_2(S_2CNMe_2)_2(C_8H_{12})$	**(11)**	3.24s		4.0–3.2m, 2.1–1.9 br m, 1.5–1.1m	1721 ($C\equiv C$), 1540 ($C\overset{...}{-}N$)
$WI_2(S_2CNEt_2)_2(C_8H_{12})$	**(12)**	1.04m		4.0–3.2m, 2.1–0.9 br m	ca. 1510 ($C\overset{...}{-}N$)
$MoO(S_2CNMe_2)_2(C_8H_{12})$	**(13)**	3.40s		3.0–2.7 br m, 2.0–1.6 br m	1852 ($C\equiv C$), 1540 ($C\overset{...}{-}N$), 920 ($Mo{=}O$)
$MoO(S_2CNEt_2)_2(C_8H_{12})$	**(14)**	1.30t	3.82q	3.1–2.6m, 2.0–1.3m	1851 ($C\equiv C$), 1504 ($C\overset{...}{-}N$), 920 ($Mo{=}O$)
$MoBr_2(CO)(C_8H_{12})(PEt_3)_2$	**(15)**	0.88m	4.5 br m[e], 1.9–1.5 br m		1920 ($C\equiv O$)
$WBr_2(CO)(C_8H_{12})(PEt_3)_2$	**(16)**	0.92m	4.35 br m[e], 1.67m		1906 ($C\equiv O$)

---

[a] Measured in $CDCl_3$, except where stated; complexes **1**, **2** and **4** were measured at 60 MHz, **5** and **6** at 100 MHz, the rest at 200 MHz. [b] Measured as Nujol mulls. [c] 1912 cm^{-1} (CH_2Cl_2). [d] NMR spectrum measured in CD_2Cl_2. [e] α-CH_2 resonance of C_8H_{12}.

TABLE 2

^{13}C NMR DATA (δ) FOR MOLYBDENUM AND TUNGSTEN CYCLOOCTYNE COMPLEXES [a]

Complex	C≡C	CO	R_2NCS_2	CH_3(dtc/PEt_3)	CH_2(dtc/PEt_3)	$CH_2(C_8H_{12})$ [b]
1	218.2	238.1	209.0, 200.8	40.8, 39.6		36.3, 27.0, 25.7
2	217.0	238.4	207.4, 199.6	12.85, 12.45, 12.36, 12.24	45.9, 44.6, 44.1	36.1, 26.9, 25.9
3	215.2	237.0	213.5, 201.8	40.8, 39.64, 39.57		36.1, 26.8, 26.4
4	214.4	237.8	212.2, 200.6	13.0, 12.58, 12.56, 12.3	45.9, 44.4, 44.1	36.1, 26.9, 26.5
5	241.2		199.5	39.1, 38.9		ca. 39, 26.5, 24.7
6	239.1		197.2	11.8, 11.7	42.3, 41.9	37.7, 25.5, 23.7
7	233.1		199.5	38.3, 37.9		37.8, 26.5, 25.4
8	227.4		not observed	12.7, 12.6	43.7, 43.17	37.8, 26.6, 25.6
9	239.8		198.5	40.1, 39.2, 38.5, 37.7		35.8, 28.9-25.2
11	239.2		200.9	42.1-37.1		27.0–25.2
13	145.5		205.2	40.65		29.3, 27.2, 26.7
14	145.9		201.6	12.5	45.6	29.4, 27.2, 26.8
15	236.0 [c]	232.0 [d]		7.6	17.5	39.0, 26.7, 25.0
16	227.8 [e]	227.0 [f]		7.8	18.0	38.6, 26.8, 25.8

[a] Measured in $CDCl_3$ containing Me_4Si as internal reference; spectra of **10** and **12** could not be measured owing to decomposition. [b] Values quoted in the order α, β, γ. [c] Average of chemical shifts of signals at δ 240.2 and 232.1 ppm observed at −50°C. [d] Triplet, $^2J(PC)$ 10.2 Hz. [e] Average of chemical shifts of signals at δ 232.5 and 227.7 ppm observed at −50°C. [f] Triplet, $^2J(PC)$ 6.4 Hz.

collapse, coalesce at ca. −45°C and reappear at ca. −60°C as doublets. The carbonyl and dtc resonances do not change in this temperature range. The rate constants for alkyne rotation, k_{ex}, at the coalescence temperature have been calculated from the simple two-site exchange formula $k_{ex} = \pi\Delta\nu/\sqrt{2}$ (Table 3). The free energies of activation, $\Delta G^{\neq}$, calculated from the usual Eyring equation, are in the range 46–50 kJ mol^{-1} and thus are very similar to those found for the same process in the analogous acyclic alkyne complexes [17].

Complexes **1**–**4** are air-stable for several weeks and do not react with typical two-electron donor ligands such as CO or PMe_2Ph; indeed, CO and PPh_3 are displaced from the coordination sphere of the metal in the preparation of the complexes. Like their acyclic alkyne counterparts, therefore, they do not behave as coordinately unsaturated 16e complexes, and this further supports the notion of four-electron donation from the alkyne. The complexes are also inert towards acids and alkyl halides, but they react with bromine or iodine, with loss of CO, to give brown, microcrystalline cyclooctyne complexes of molybdenum(IV) and tungsten(IV) (**5**–**12**) (eq. 2).

$$M(S_2CNR_2)_2(CO)(C_8H_{12}) + X_2 \rightarrow MX_2(S_2CNR_2)_2(C_8H_{12}) + CO \tag{2}$$

(M = Mo; X = Br; R = Me (**5**), Et (**6**)
M = W; X = Br; R = Me (**7**), Et (**8**)
M = Mo, X = I; R = Me (**9**), Et (**10**)
M = W, X = I; R = Me (**11**), Et (**12**))

The reactions with iodine occur smoothly at room temperature, whereas those with bromine must be carried out at −78°C. At room temperature, the molybdenum

TABLE 3

APPROXIMATE ACTIVATION BARRIERS TO FLUXIONAL PROCESSES IN CYCLOOCTYNE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

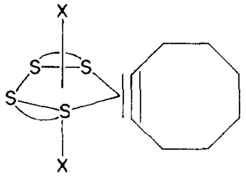
Complex		T_c (K)	Site probed	$\Delta G^{\neq}$ (kJ mol^{-1}) [a]
$Mo(S_2CNMe_2)_2(CO)(C_8H_{12})$	(**1**)	218	α-CH_2	42.8
		228	C≡C	44.0
$Mo(S_2CNEt_2)_2(CO)(C_8H_{12})$	(**2**)	228	α-CH_2	45.0
$W(S_2CNMe_2)_2(CO)(C_8H_{12})$	(**3**)	233	α-CH_2	45.5
$W(S_2CNEt_2)_2(CO)(C_8H_{12})$	(**4**)	233	C≡C	44.3
		228	α-CH_2	44.6
$MoO(S_2CNMe_2)_2(C_8H_{12})$	(**13**)	288	C≡C	56.1
		273	α-CH_2	55.9
		258	β-CH_2	56.0
		278	CH_3	55.4
$MoO(S_2CNEt_2)_2(C_8H_{12})$	(**14**)	293	C≡C	57.0
		278	α-CH_2	56.6
		278	CH_2(Et)	56.3
$MoBr_2(CO)(C_8H_{12})(PEt_3)_2$	(**15**)	263	α-CH_2	54.5
$WBr_2(CO)(C_8H_{12})(PEt_3)_2$	(**16**)	273	α-CH_2	53.0

[a] Calculated at the coalescence temperature from the equation $\Delta G^{\neq} = \pi\Delta\nu/\sqrt{2}$.

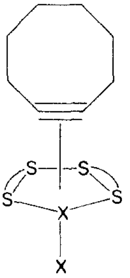
complexes react violently with bromine giving impure products, while the tungsten compounds under the same conditions lose both cyclooctyne and CO to give the known dibromides $WBr_2(S_2CNR_2)_2$ (R = Me, Et) [25].

The IR spectra of **5–12** contain a band in the region 1720–1750 cm^{-1} that can be assigned to $\nu(C\equiv C)$ modified by coordination (Table 1). The $^{13}C\{^1H\}$ NMR spectra (Table 2) show two sets of signals for each alkyl group on the dtc ligand but only one resonance for the trigonal carbon atoms, suggesting that the dtc ligands are equivalent but that their alkyl groups are in different environments. Only four cyclooctyne carbon resonances due to the alkyne carbon and the α-, β- and γ-CH_2 groups are observed and the spectra do not change on cooling to −100°C. Thus, unless alkyne rotation is still fast on the NMR time scale at this temperature, the observations indicate that there is a plane of symmetry that bisects the alkyne $C\equiv C$ bond and passes between the two dtc ligands.

The coordinated alkyne carbons in **5–8** are even less shielded than those of **1–4** (δ ca. 230–240 ppm), implying that cyclooctyne is still donating four electrons so that the metal atom in these compounds retains its 18e configuration. Since analogous molybdenum(IV) or tungsten(IV) complexes of acyclic alkynes are unknown, structural precedents are lacking. If cyclooctyne is regarded as occupying one coordination site, the complexes are formally seven-coordinate. Structures consistent with the spectroscopic data are II and III, both of which are based on a pentagonal bipyramid [26]. Structure III, with *cis*-chlorine atoms, is similar to that established by X-ray crystallography for the phenylimido complex $Mo(NPh)Cl_2(S_2CNEt_2)_2$ [27].



II

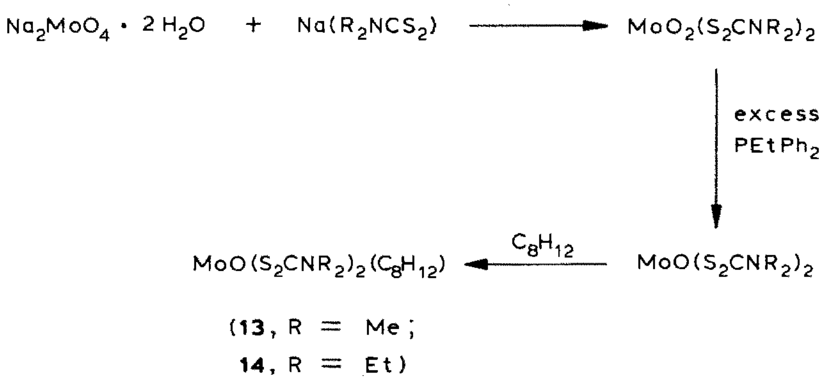


III

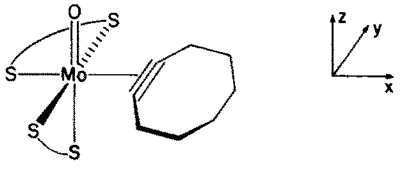
S—S = Me_2NCS_2, Et_2NCS_2
X = Br, I
M = Mo, W

The crude products obtained by reaction of **2** or **4** with chlorine at −78°C showed $C\equiv C$ bands in their IR spectra at 1754 and 1741 cm^{-1}, respectively, suggesting that the compounds $MCl_2(S_2CNEt_2)_2(C_8H_{12})$ had been formed, but these could not be isolated in a pure state.

Yellow, microcrystalline oxomolybdenum(IV) cyclooctyne complexes $MoO(S_2CNR)_2)_2(C_8H_{12})$, **13** and **14**, are readily formed by the reaction of cyclooctyne with $MoO(S_2CNR_2)_2$, as shown in Scheme 1. Their IR spectra show a weak band at ca. 1850 cm^{-1} due to $\nu(C\equiv C)$ of the coordinated alkyne and an intense band at ca. 920 cm^{-1} due to $\nu(Mo{=}O)$, the latter being ca. 30 cm^{-1} lower than the value observed in the parent five-coordinate complexes $MoO(S_2CNR_2)_2$. These properties are similar to those of the corresponding complexes of acyclic alkynes [16,18]. However, in contrast to the complexes of C_2H_2, PhC_2H and PhC_2Ph, complexes **13** and **14** show no tendency to lose the coordinated alkyne and they seem to be at least as stable as the corresponding complexes of the highly electrophilic acetylenes $CF_3C_2CF_3$, $MeO_2CC_2CO_2Me$ and p-$MeC_6H_4COC_2COC_6H_4Me$-p. By analogy with $MoO(S_2CNMe_2)_2(MeO_2CC_2CO_2Me)$, the structure of which has been determined by X-ray crystallography [18], complexes **9** and **10** are assumed to be distorted octahedral, the dtc ligands being mutually *cis* and the alkyne lying in a plane perpendicular to that of the Mo=O group (structure IV). This arrangement, which has also been found for the related oxometal(IV) alkyne complexes $MoO(\eta$-$C_5H_5)(SC_6F_5)(CF_3C_2CF_3)$ [28] and $WO(\eta$-$C_5H_5)(Ph)(PhC_2Ph)$ [29], differs from that in the carbonyl complexes **1–4** because the oxo ligand is a π-donor rather than

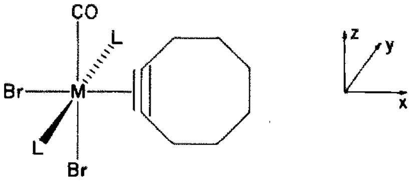


SCHEME 1. Formation of $MoO(S_2CNR_2)_2(C_8H_{12})$.



IV

S—S = Me_2NCS_2, Et_2NCS_2



V

L = PEt_3
M = Mo, W

a π-acceptor. An orientation parallel to the Mo=O bond would give rise to a repulsive interaction between the filled metal d_{xy} orbital and the filled $\pi_\perp$ alkyne orbital, whereas the 90° orientation allows overlap of the filled $\pi_\perp$ alkyne orbital with the empty metal d_{xz} orbital [18,22,28]. However, there is competition for the latter from the filled p_x orbital of the oxo ligand. This probably accounts for the facts that ν(C≡C) is higher for **13** and **14** than for either **1**–**4** or **5**–**12** and that the alkyne carbons in **13** and **14** (δ ca. 146 ppm) are more shielded than those in **1**–**4**. The results suggest that cyclooctyne, like acyclic alkynes, can be regarded as donating approximately 3π-electrons in complexes **13** and **14** [18,19].

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **13** and **14** (Tables 1 and 2) show that the dtc ligands are apparently equivalent on the NMR time scale at room temperature, in contrast with those of **1**–**4**. Also, there are only four cyclooctyne ^{13}C resonances at room temperature, indicative of a time-averaged plane of symmetry bisecting the coordinated C≡C bond. On cooling to −50°C, the cyclooctyne ^{13}C resonances split into doublets and the singlets due to the dtc carbons split into four lines, as expected on the basis of structure IV. The activation barrier to the fluxional process at the coalescence temperature (Table 3) is ca. 55 kJ mol^{-1} and, in the case of **14**, is the same for the cyclooctyne and for the dtc ligands. A similar barrier has been derived from the variable ^{1}H NMR spectra of similar oxotungsten(IV) complexes of acyclic alkynes and it has been suggested [20] that one-ended dissociation of a dtc ligand induced by the high *trans*-influence of the oxo ligand generates a fluxional five-coordinate intermediate.

Cyclooctyne also reacts at room temperature with the divalent metal complexes $MoBr_2(CO)_2(PEt_3)_2$ and $WBr_2(CO)_3(PEt_3)_2$ to give green $MoBr_2(CO)(C_8H_{12})(PEt_3)_2$ (**15**) and violet $WBr_2(CO)(C_8H_{12})(PEt_3)_2$ (**16**) respectively in yields of ca. 70%. In contrast to the dtc compounds **1**–**4**, these triethylphosphine complexes do not react further with cyclooctyne. Their IR spectra (Table 1) show a single ν(CO) band at ca. 1900 cm^{-1} but, as with **1**–**4**, no band assignable to ν(C≡C) could be located. The compounds probably have an essentially octahedral structure V similar to that found by X-ray crystallography for the corresponding phenylacetylene complex $MoBr_2(CO)(PhC_2H)(PEt_3)_2$ [30], in which the triethylphosphine ligands are mutually *trans* and the coordinated C≡C bond is parallel to the M–CO axis, as in **1**–**4**. The presence of ^{31}P NMR singlets at δ 9.6 and −0.3 ppm (relative to 85% H_3PO_4) in **15** and **16** confirms that the phosphorus atoms are equivalent. The chemical shift value for **15** is very similar to that observed for the analogous but-2-yne complex (δ 9.1 ppm) [30]. The singlet for **16** shows satellites (J 234 Hz) due to coupling with ^{183}W ($I = \frac{1}{2}$; 14.4% abundance).

At room temperature, the ^{13}CO resonances of **15** and **16** are triplets at δ ca. 230 ppm and there are three singlets due to the cyclooctyne CH_2 groups. The alkyne ^{13}C resonances cannot be observed because they happen to coalesce at about room temperature. On cooling to −50°C, the cyclooctyne CH_2 resonances become doublets and the C≡C resonances now appear as a pair of ill-resolved triplets in the region δ 225–240 ppm characteristic of four π-electron donation from the alkyne; the ^{13}CO resonance remains unchanged. The activation barrier to cyclooctyne rotation, estimated from the coalescence temperature for the α-CH_2 resonance, is ca. 55 kJ mol^{-1} in both **15** and **16**, and thus is similar to the values found for $MoBr_2(CO)(MeC_2Me)(PEt_3)_2$ [30] and for the dtc complexes **1**–**4**.

Attempts to oxidize **15** and **16** with bromine to the corresponding tetravalent metal complexes $MBr_2(C_8H_{12})(PEt_3)_2$ have yielded very moisture-sensitive solids which have not yet been satisfactorily characterized.

Discussion

The complexes of cyclooctyne with divalent and tetravalent molybdenum and tungsten resemble those formed by acyclic alkynes, but are generally more stable, especially in the higher oxidation state. This is evident from the failure of the oxomolybdenum(IV) complexes $MoO(S_2CNR_2)_2(C_8H_{12})$ to undergo dissociation of cyclooctyne and from the fact that the divalent metal complexes $M(S_2CNR_2)_2$-$(CO)(C_8H_{12})$ can be oxidized by halogens without loss of cyclooctyne.

The strain energy of cyclooctyne has been estimated as 55 kJ mol^{-1} on the basis of an electron diffraction study of the gaseous molecule [31]. It includes contributions from a lengthening of the C≡C bond to 1.232(6) Å from its normal value of 1.202(5) Å [32], an angle deformation of ca. 21° at the alkyne carbon atoms, elongations and compressions of the aliphatic C–C bonds, and methylene hydrogen atom repulsions. An X-ray crystallographic study of $Pt(C_8H_{12})(PPh_3)_2$ has shown that the complexed C≡C bond is further lengthened to 1.279(13) Å and that the substituents at the alkyne carbon atoms are bent back from the C≡C bond by ca. 14° more than in free cyclooctyne [33]. These general features, which are characteristic of alkyne coordination [34], are likely to occur in the molybdenum and tungsten complexes reported here (see, for example, the structure of $W(S_2CNEt_2)_2(CO)(C_2H_2)$ [14] and $MoO(S_2CNMe_2)_2(C_8H_{12})$ [18]). Thus the inreased stability of the cyclooctyne complexes relative to those of, for example, but-2-yne is undoubtedly associated with relief of strain in the eight-membered ring on complexation.

The similarity of the ^{13}C chemical shifts and of the activation barriers to rotation of coordinated cyclooctyne to those of acyclic alkynes in corresponding complexes suggests that the metal–alkyne bonds in the cyclooctyne complexes and in the acyclic alkyne complexes do not differ much in nature. The previously noted correlation of ^{13}C chemical shifts with number of π-electrons donated [19] is also evident in the cyclooctyne complexes and the greatly reduced shielding in the $MX_2(S_2CNR_2)_2(C_8H_{12})$ complexes compared with that in $MoO(S_2CNR_2)_2(C_8H_{12})$ is consistent with donation of, respectively, four and three π-electrons from cyclooctyne. As expected, therefore, two halide ligands do not perform as well as an oxo ligand in the competition with the alkyne for vacant metal *d*-orbitals.

Experimental

IR spectra were measured on a Perkin–Elmer 683 spectrometer and were calibrated against polystyrene. Proton and carbon-13 NMR spectra were measured on JEOL FX200 or Bruker CXP200 spectrometers (^{13}C at 50.10 and 50.29 MHz respectively), tetramethylsilane being the internal reference. Some proton NMR spectra were measured on JEOL PMX 60 or JEOL MH 100 instruments. Phosphorus-31 NMR spectra were recorded at 24.3 MHz on a JEOL FX60 spectrometer, the external reference being 85% H_3PO_4. Melting points were measured in open capillaries and are uncorrected. Analyses and molecular weight determinations were carried out by the ANU Analytical Service (Miss Brenda Stevenson and associates). Spectroscopic data are collected in Tables 1 (IR, ^1H NMR) and 2 (^{13}C), analytical data are in Table 4.

Solvents were routinely dried and degassed by standard techniques before use. All manipulations were performed under argon or nitrogen with use of standard Schlenk techniques.

TABLE 4

ANALYTICAL DATA AND MELTING POINTS FOR CYCLOOCTYNE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Complex		M.p. (°C)	Found (calcd.)(%)			
			C	H	N	Other
$Mo(S_2CNMe_2)_2(CO)(C_8H_{12})$	**(1)**	161–162	38.4	5.2	5.7	S:26.7
			(38.1)	(5.1)	(5.9)	(27.1)
$Mo(S_2CNEt_2)_2(CO)(C_8H_{12})$	**(2)** [a]	100–101	43.1	6.2	5.1	S:23.8
			(43.2)	(6.1)	(5.3)	(24.3)
$W(S_2CNMe_2)_2(CO)(C_8H_{12})$	**(3)**	174–176	32.1	4.2	4.8	S:22.7
			(32.15)	(4.3)	(5.0)	(22.9)
$W(S_2CNEt_2)_2(CO)(C_8H_{12})$	**(4)**	107–108	37.5	5.3	4.4	S:20.5
			(37.0)	(5.2)	(4.5)	(20.8)
$MoBr_2(S_2CNMe_2)_2(C_8H_{12})$	**(5)**	122(dec)	28.5	3.75	4.4	[b]
			(27.8)	(4.0)	(4.6)	
$MoBr_2(S_2CNEt_2)_2(C_8H_{12})$	**(6)**	157(dec)	32.4	5.0	4.1	Br [c] 22.0
			(32.7)	(4.9)	(4.2)	(24.2)
$WBr_2(S_2CNMe_2)_2(C_8H_{12})$	**(7)**	165(dec)	24.45	3.6	3.9	Br [c]:21.7
			(24.3)	(3.5)	(4.05)	(23.1)
$WBr_2(S_2CNEt_2)_2(C_8H_{12})$	**(8)**	162(dec)	28.9	4.4	3.5	Br [c]:21.2
			(28.9)	(4.3)	(3.7)	(21.4)
$MoI_2(S_2CNMe_2)_2(C_8H_{12})$	**(9)**	100	24.3	3.3	3.8	I [c]:34.3
			(24.1)	(3.5)	(4.0)	(36.3)
$MoI_2(S_2CNEt_2)_2(C_8H_{12})$	**(10)**	160(dec)	27.9	3.9	3.8	
			(28.7)	(4.3)	(3.7)	
$WI_2(S_2CNMe_2)_2(C_8H_{12})$	**(11)**	160(dec)	21.4	2.9	3.6	I:33.2
			(21.4)	(3.1)	(3.6)	(32.3)
$WI_2(S_2CNEt_2)_2(C_8H_{12})$	**(12)** [b]	90	25.5	3.7	2.8	[b]
			(25.7)	(3.8)	(3.3)	
$MoO(S_2CNMe_2)_2(C_8H_{12})$	**(13)**	194(dec.)	36.6	5.3	6.0	
			(36.5)	(5.25)	(6.1)	
$MoO(S_2CNEt_2)_2(C_8H_{12})$	**(14)**	128–129	41.45	6.0	5.4	S:24.4
			(41.85)	(6.2)	(5.4)	(24.8)
$MoBr_2(CO)(C_8H_{12})(PEt_3)_2$	**(15)**	86	40.6	6.8	10.0	Br:25.25
			(40.15)	(6.7)	(9.9) [d]	(25.4)
$WBr_2(CO)(C_8H_{12})(PEt_3)_2$	**(16)**	80(dec.)	35.4	5.6	7.9	Br:20.7
			(35.2)	(5.9)	(8.65) [d]	(22.3)

[a] Mol. wt. (osmometry in CH_2Cl_2 at 27°C): Found: 535; calcd.: 529. [b] Analyses for S and halogen were irreproducible and generally 10–25% less than calculated. [c] Analysis for S was irreproducible and ca. 20% less than calculated. [d] Analysis for P.

Starting materials

The compounds $Na(Me_2NCS_2)\cdot 2H_2O$, $Na(Et_2NCS_2)\cdot 3H_2O$, $Mo(CO)_6$, $W(CO)_6$ and triethylphosphine were obtained from commercial suppliers. Cyclooctyne was prepared by reaction of SeO_2 with cyclooctanone semicarbazone and pyrolysis of the resulting cyclooctano-1,2,3-selenadiazole [35,36]. Literature procedures were used to prepare $W(CO)_3(S_2CNMe_2)_2$ from $W(CO)_6$ [25,37,38]. Attempts to make $Mo(CO)_3(S_2CNR_2)_2$ (R = Me, Et) similarly from $Mo(CO)_6$ gave a mixture containing mainly the dicarbonyl, together with the tricarbonyl and some insoluble material. The complexes $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$ (R = Me, Et) were therefore prepared as described below; these preparations are based on literature procedures [39–41].

(1) To a slurry of $Mo(CO)_n(S_2CNMe_2)_2$ ($n \sim 2$) (2.0 g, ca. 5 mmol) in dichloromethane (70 ml) was added a solution of triphenylphosphine (1.44 g, 5.5 mmol) in dichloromethane (30 ml). The mixture was stirred for 1 h, filtered, and the filtrate was evaporated to ca. 20 ml volume. Methanol (50 ml) was added, the mixture was evaporated to ca. half volume, and cooled to −20°C. The orange precipitate of *$Mo(S_2CNMe_2)_2(CO)_2(PPh_3)$* was filtered off, washed with methanol, and dried in vacuo. Yield: 1.95 g (61%).

(2) A solution of $Na(Me_2NCS_2)\cdot 2H_2O$ (0.54 g, 2.84 mmol) in methanol (35 ml) was added dropwise to a vigorously stirred solution of $MoCl_2(CO)_3(PPh_3)_2$ (1.0 g, 1.29 mmol). The mixture was evaporated to ca. 30 ml and cooled to −20°C. The orange solid was isolated as in (1) to give 0.84 g (95%) of product.

The corresponding diethyldithiocarbamato complexes were made similarly.

The molybdenum complex $MoBr_2(CO)_2(PEt_3)_2$ has been made by the action of bromine on $Mo(CO)_4(PEt_3)_2$ [42]. The tungsten compound $WBr_2(CO)_3(PEt_3)_2$ has not been reported previously, although the PMe_2Ph analogue has been prepared by bromination of $W(CO)_4(PEt_3)_2$ [42]. We used the simpler method described below.

A solution of bromine (1.46 ml, 28.4 mmol) in dichloromethane (10 ml) was added slowly to a slurry of $W(CO)_6$ (10 g, 28.4 mmol) in dichloromethane (50 ml) cooled to −78°C. The resulting brown mixture containing $[WBr_2(CO)_4]_2$ was stirred for 15 min, allowed to warm to room temperature, and filtered into a solution of triethylphosphine (8.4 ml, 56.8 mmol) in methanol (50 ml). The brown solution was evaporated to ca. 20 ml, thus causing a yellow solid to precipitate. After the solution had been set aside at −20°C overnight, the solid was filtered off, washed with methanol, and dried in vacuo to give 5.89 g (31%) of *$WBr_2(CO)_3(PEt_3)_2$*. The yield could probably be improved by using a larger volume of dichloromethane in the preparation of $[WBr_2(CO)_4]_2$.

A similar procedure using $Mo(CO)_6$ in place of $W(CO)_6$ gave a green solution which, on evaporation and cooling to −20°C, gave a yellow solid, probably $MoBr_2(CO)_3(PEt_3)_2$. In vacuo this lost CO to give blue *$MoBr_2(CO)_2(PEt_3)_2$* in 30% yield.

Cyclooctyne complexes

Bis(dimethyldithiocarbamato)(carbonyl)(cyclooctyne)tungsten(II), $W(S_2CNMe_2)_2(CO)(C_8H_{12})$ (3)

Cyclooctyne (101 μl, 1.38 mmol) was added to a solution of $W(S_2CNMe_2)_2(CO)_3$ (0.70 g, 1.38 mmol) in THF (30 ml) to give immediately a bright green solution. The solution was evaporated to ca. 5 ml and ethanol (ca. 30 ml) was added dropwise until solid just began to precipitate. The mixture was set aside at −20°C overnight and the green microcrystalline product was filtered off, washed with cold ethanol, and dried in vacuo. The yield was 0.56 g (72%).

The corresponding diethyldithiocarbamato complex $W(S_2CNEt_2)_2(CO)(C_8H_{12})$ (**4**) was obtained similarly in 52% yield; in this case the THF/ethanol solution had to be evaporated under reduced pressure to induce the product to precipitate. The molybdenum complexes $Mo(S_2CNR_2)_2(CO)(C_8H_{12})$ (R = Me (**1**), Et (**2**)) were obtained similarly in yields of ca. 50% from $Mo(S_2CNR_2)_2(CO)_2(PPh_3)$.

Bis(diethyldithiocarbamato)(cyclooctyne)dibromomolybdenum(IV), $MoBr_2(S_2CNEt_2)_2(C_8H_{12})$ *(**6**)*

A solution of $Mo(S_2CNEt_2)_2(CO)(C_8H_{12})$ (**2**) in THF prepared in situ as described above was cooled to −78°C and treated dropwise with a solution of bromine (1 mol per mol of complex) in dichloromethane (10 ml). The brown solution was stirred for 10 min and allowed to warm to room temperature. The volume of solution was reduced to ca. 5 ml and propan-2-ol (30 ml) was added. Evaporation to ca. 20 ml volume and cooling to −20°C gave a brown solid. After filtration, washing successively with cold propan-2-ol and ether, and drying in vacuo, the yield of **6** was 60%.

The dimethyldithiocarbamato analogue (**5**) was prepared similarly in 60% yield, the final product being heated at 65°C in vacuo overnight to remove traces of propan-2-ol.

Bis(diethyldithiocarbamato)(cyclooctyne)dibromotungsten(IV), $WBr_2(S_2CNEt_2)_2(C_8H_{12})$ *(**8**)*

Treatment of a solution of $W(S_2CNEt_2)_2(CO)_3$ in CH_2Cl_2 first with cyclooctyne, and then with bromine at −78°C, as for **3**, gave a brown solution. This was evaporated to dryness and the residue was triturated with acetonitrile to give the brown microcrystalline product in 50% yield.

The analogous S_2CNMe_2 complex **7** was prepared similarly in 68% yield, except that the residue was triturated with ether.

Bis(dimethyldithiocarbamato)(cyclooctyne)diiodotungsten(IV), $WI_2(S_2CNMe_2)_2(C_8H_{12})$ *(**11**)*

A solution of **3** prepared in situ in dichloromethane as described above was treated with iodine (1 mol per mol of complex) at room temperature to give a red-brown solution. This was evaporated to ca. 5 ml and ether (ca. 20 ml) was added, thus precipitating an oily solid. The supernatant liquid was decanted and the oily solid was triturated with ether to give the product as a red solid in 61% yield. This can be recrystallized from dichloromethane/ether.

The complex $WI_2(S_2CNEt_2)_2(C_8H_{12})$ (**12**) was prepared similarly as red-brown microcrystals in 58% yield; in this case, pentane rather than ether was used to triturate the residue.

Bis(dimethyldithiocarbamato)(cyclooctyne)diiodomolybdenum(IV), $MoI_2(S_2CN(Me_2)_2(C_8H_{12})$ *(**9**)*

A solution of **1** in CH_2Cl_2 was treated with 1 mol equiv. of iodine at room temperature to give a brown solution. This was evaporated to dryness and the residue was recrystallized from CH_3CN/CH_3OH to give **9** in 50% yield as a red-brown solid.

The analogous brown, microcrystalline diethyldithiocarbamato complex **10** was obtained similarly, the yield after recrystallization from dichloromethane/ether being 28%.

Bis(diethyldithiocarbamato)(cyclooctyne)oxomolybdenum(IV), $MoO(S_2CNEt_2)_2(C_8H_{12})$ *(14)*

Cyclooctyne (153 μl, 1.22 mmol) was added to a solution of $MoO(S_2CNEt_2)_2$ (0.50 g, 1.22 mmol) in dichloromethane (20 ml). The golden-yellow solution was evaporated to dryness and the residue was triturated with ether. Recrystallization of the solid from acetonitrile gave 0.32 g (50%) of yellow, crystalline **14**.

Similar treatment of $MoO(S_2CNMe_2)_2$ produced a green solid which, after recrystallization from CH_2Cl_2/CH_3CN, gave yellow microcrystals of $MoO(S_2CNMe_2)_2(C_8H_{12})$ (**13**) in 60% yield.

Bis(triethylphosphine)(carbonyl)(cyclooctyne)dibromotungsten(II), $WBr_2(CO)(C_8H_{12})(PEt_3)_2$ *(16)*

Cyclooctyne (127 μl, 1.02 mmol) was added to a solution of $WBr_2(CO)_3(PEt_3)_2$ (0.68 g, 1.02 mmol) in dichloromethane (10 ml). The colour changed to violet over a period of 30 min. Evaporation to dryness and trituration of the residue with pentane gave the mauve, microcrystalline product (0.51 g, 70%).

The complex $MoBr_2(CO)(C_8H_{12})(PEt_3)_2$ (**15**) was prepared analogously from $MoBr_2(CO)_2(PEt_3)_2$ in 70% yield as green microcrystals.

References

1 A. Krebs, in H.G. Viehe (Ed.), Chemistry of Acetylenes, Marcel Dekker, New York, 1969, Chapter 15, p. 987.

2 M. Nakagawa in S. Patai (Ed.), The Chemistry of the Carbon–Carbon Triple Bond, Part 2, Wiley-Interscience, 1978, Chapter 15, p. 635.

3 G. Wittig and S. Fischer, Chem. Ber., 105 (1972) 3542.

4 T.L. Gilchrist, F.J. Graveling and C.W. Rees, Chem. Comm., (1968) 821.

5 M.A. Bennett and T. Yoshida, J. Am. Chem. Soc., 100 (1978) 1750.

6 H. Kolshorn, H. Meier and E. Müller, Tetrahedron Lett., (1972) 1589.

7 G. Wittig and P. Fritze, Liebigs Ann. Chim., 712 (1968) 79.

8 H. Meier, J. Heiss, H. Suhr and E. Müller, Tetrahedron, 24 (1968) 2307.

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

10 M.A. Bennett and P.B. Donaldson, Inorg. Chem., 17 (1978) 1995.

11 H. Petersen and H. Meier, Nouv. J. Chim., 4 (1980) 687.

12 J.W. McDonald, J.L. Corbin and W.E. Newton, J. Am. Chem. Soc., 97 (1975) 1970.

13 J.W. McDonald, W.E. Newton, C.T.C. Creedy and J.L. Corbin, J. Organomet. Chem., 92 (1975) C27.

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

15 E.A. Maatta, R.A.D. Wentworth, W.E. Newton, J.W. McDonald and G.D. Watt, J. Am. Chem. Soc., 100 (1978) 1320.

16 E.A. Maatta and R.D. Wentworth, Inorg. Chem., 18 (1979) 524.

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

18 W.E. Newton, J.W. McDonald, J.L. Corbin, L. Ricard and R. Weiss, Inorg. Chem., 19 (1980) 1997.

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

20 J.L. Templeton, B.C. Ward, G.J.-J. Chen, J.W. McDonald and W.E. Newton, Inorg. Chem., 20 (1981) 1248.

21 R.S. Herrick and J.L. Templeton, Organometallics, 1 (1982) 842.
22 J.L. Templeton, P.B. Winston and B.C. Ward, J. Am. Chem. Soc., 103 (1981) 7713.
23 K. Tatsumi, R. Hoffmann and J.L. Templeton, Inorg. Chem., 21 (1982) 466.
24 M.A. Bennett, I.W. Boyd, G.B. Robertson and W.A. Wickramasinghe, J. Organomet. Chem., 290 (1985) 181.
25 G.L. Hillhouse and B.L. Haymore, J. Am. Chem. Soc., 104 (1982) 1537.
26 M.G.B. Drew, Prog. Inorg. Chem., 23 (1977) 67; D.L. Kepert, ibid., 25 (1979) 42.
27 E.A. Maatta, B.L. Haymore and R.A.D. Wentworth, Inorg. Chem., 19 (1980) 1055.
28 J.A.K. Howard, R.F.D. Stansfield and P. Woodward, J. Chem. Soc., Dalton Trans., (1976) 246.
29 N.G. Bokiy, Yu.V. Gatilov, Yu.T. Struchkov and N.A. Ustynyuk, J. Organomet. Chem., 54 (1973) 213.
30 P.B. Winston, S.J. Nieter Burgmayer and J.L. Templeton, Organometallics, 2 (1983) 167.
31 J. Haase and A. Krebs, Z. Naturforsch. A, 26 (1971) 1190.
32 Chem. Soc. Spec. Publ. No. 18, p. S16s.
33 G.B. Robertson and P.O. Whimp, Aust. J. Chem., 33 (1980) 1373.
34 S. Otsuka and A. Nakamura, Adv. Organomet. Chem., 14 (1976) 245.
35 H. Meier and E. Voigt, Tetrahedron, 28 (1972) 187.
36 I. Lalezari, A. Shafiee and M. Yalpani, J. Heterocycl. Chem., (1972) 1411.
37 J.L. Templeton and B.C. Ward, Inorg. Chem., 19 (1980) 1753.
38 J.A. Broomhead and C.G. Young, Aust. J. Chem., 35 (1982) 277.
39 R. Colton and G.G. Rose, Aust. J. Chem., 23 (1970) 1111.
40 G.J.-J. Chen, R.O. Yelton and J.W. McDonald, Inorg. Chim. Acta, 22 (1977) 249.
41 J.L. Templeton and B.C. Ward, J. Am. Chem. Soc., 103 (1981) 3743.
42 J.R. Moss and B.L. Shaw, J. Chem. Soc. (A), (1970) 595.