

1,8-Cyclotetradecadiyne complexes of molybdenum(II) and tungsten(II)

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Abstract

The complexes $[\text{Ml}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ and W) react with an equimolar amount of 1,8-cyclotetradecadiyne (1,8-CTDiyne) in CH_2Cl_2 at room temperature to give the new bisalkyne complexes $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ in good yield. ^{13}C NMR spectroscopy confirms that 1,8-CTDiyne is coordinated as a bisalkyne ligand in these complexes. The complex $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ reacts with $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$ (dppm) in refluxing chloroform (48 h) to give the complex $[\text{Wl}_2(\text{CO})(\text{dppm})(\eta^2\text{-1,8-CTDiyne})]$ where the 1,8-CTDiyne is bonded via one of its alkyne functional groups. ^{13}C NMR spectroscopy indicates that the alkyne ligand in this complex is donating 4-electrons to the tungsten. The compounds $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ also react with one equivalent ($\text{M} = \text{W}$) and two equivalents ($\text{M} = \text{Mo}$) of $\text{CyN}=\text{CHCH}=\text{NCy}$ in CH_2Cl_2 to give the novel monocationic complexes $[\text{Wl}(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]\text{I} \cdot \text{Et}_2\text{O}$ and $[\text{Mol}(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiyne})]\text{I}$. The preparations of the new monoalkyne complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})_2(\eta^2\text{-1,8-CTDiyne})]$ ($\text{X} = \text{NEt}_2$ and NC_4H_8) are also described.

Introduction

Reactions of macrocyclic alkadiynes with organotransition-metal complexes have most commonly resulted in the formation of cyclobutadiene complexes via the intramolecular transannular cyclization of the diynes [1,2]. The intramolecular transannular cyclization of macrocyclic alkadiynes with metal carbonyls has been proposed to proceed via a metallocyclopentadiene intermediate [3,4], which must be preceded by the formation of a bisalkyne complex. Hitherto, no mononuclear bisalkyne complexes containing macrocyclic alkadiynes (such as 1,8-cyclotetradecadiyne) have been reported.

In view of these observations and the wide variety of bisalkyne complexes of molybdenum(II) and tungsten(II) previously reported [5–14]. It was decided to

investigate the reactions of our highly versatile complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) with a macrocyclic diyne, namely 1,8-cyclotetradecadiyne. The results of this work are described in this paper.

Results and discussion

Equimolar quantities of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) and 1,8-cyclotetradecadiyne (1,8-CTDiyne) react in CH_2Cl_2 at room temperature to give good yields of the new bisalkyne complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ (**1** and **2**). The complex $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ (**2**) reacts with $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$ (dppm) in refluxing CHCl_3 to give a good yield of the green monoalkyne compound $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-1,8-CTDiyne})]$ (**3**). However, reaction of **1** and **2** with one equivalent ($\text{M} = \text{W}$) or two equivalents ($\text{M} = \text{Mo}$) of $\text{CyN}=\text{CHCH}=\text{NCy}$ in CH_2Cl_2 at room temperature afforded high yields of the novel monocationic complexes $[\text{WI}(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]\text{I} \cdot \text{Et}_2\text{O}$ (**4**) and $[\text{MoI}(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiyne})]\text{I}$ (**5**). Compound **2** also reacts with two equivalents of $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ and $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$ in CH_2Cl_2 to give good yields of the monoalkyne complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})_2(\eta^2\text{-1,8-CTDiyne})]$ (**6** and **7**) ($\text{X} = \text{NEt}_2$ and NC_4H_8). All the new complexes (**1**–**7**) were fully characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2), ^1H and ^{13}C NMR spectroscopy (Tables 3 and 4). The complex $[\text{WI}(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]\text{I} \cdot \text{Et}_2\text{O}$ was confirmed as a diethyl ether solvate by repeated elemental analyses and ^1H and ^{13}C NMR spectroscopy.

It is noteworthy that reaction of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ with 1,8-CTDiyne in CH_2Cl_2 results in the formation of orange ($\text{M} = \text{Mo}$) or yellow ($\text{M} = \text{W}$) precipitates. This is in contrast to the reactions of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equiv-

Table 1

Physical and analytical data for $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ and derivatives

Complex	Colour	Yield of pure product (%)	Analysis (Found (calcd.)(%))		
			C	H	N
(1) $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$	orange	99	33.7 (33.6)	3.7 (3.8)	2.2 (2.3)
(2) $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$	yellow	93	29.5 (29.4)	3.3 (3.3)	1.6 (2.0)
(3) $[\text{WI}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-1,8-CTDiyne})]$	green	51	46.4 (46.3)	4.5 (4.1)	–
(4) $[\text{WI}(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]\text{I} \cdot \text{Et}_2\text{O}$	brown (41.8)	71 (5.7)	42.0 (3.0)	6.0	3.4
(5) $[\text{MoI}(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiyne})]\text{I}$	brown	79	51.0 (51.5)	7.4 (7.0)	5.7 (5.7)
(6) $[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)_2(\eta^2\text{-1,8-CTDiyne})]$	green	42	42.7 (43.1)	5.9 (5.8)	4.0 (4.0)
(7) $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)_2(\eta^2\text{-1,8-CTDiyne})]$	green	69	42.7 (43.4)	5.2 (5.2)	3.7 (4.0)

Table 2

IR data ^a for [MI₂(CO)(NCMe)($\eta^2, \eta^{2'}$ -1,8-CTDiyne)] and derivatives

Complex	$\nu(\text{C=O})$ (cm ⁻¹)	$\nu(\text{C}\equiv\text{C})$ (cm ⁻¹) (coordinated)
1	2032(s)	1840(vw)
2	2050(s)	1820(vw)
3	1920(s)	1655(vw)
4	2035(s)	1815(w)
5	—	1750(vw)
6	1890(s)	1780(vw)
7	1885(s)	1620(vw)

^a Run as CHCl₃ films between NaCl plates.

Table 3

¹H NMR data for [MI₂(CO)(NCMe)($\eta^2, \eta^{2'}$ -1,8-CTDiyne)] and derivatives

Complex	¹ H (δ , ppm)
1	2.52 (bs, 8H, $\equiv\text{CCH}_2$); 2.08 (bm, 15H, CH_2 and NCMe)
2	2.50 (bs, 8H, $\equiv\text{CCH}_2$); 2.08 (bm, 15H, CH_2 and NCMe)
3	7.31 (bs, 20H, <i>Ph</i>); 2.2 (bs, 8H, $\equiv\text{CCH}_2$); 1.54 (bs, 14H, CH_2 and Ph_2PCH_2)
4	7.81 (s, 2H, <i>CH</i>); 3.55, (q, $J_{7,7}$ Hz, 4H, CH_2); 1.72 (bm, 22H, <i>Cy</i> ; 20H, CH_2 ; 6H, CH_3)
5 ^a	7.73 (s, 4H, <i>CH</i>); 2.20 (bm, 20H, CH_2); 1.75 (bm, 44H, <i>Cy</i>)
6	3.78, 3.67 (q, $J_{6,5}$ Hz, 8H, CH_2); 1.21 (bm, 12H, CH_3 ; 20H, CH_2)
7	3.79, 3.69 (q, $J_{5,9}$ Hz, 16H, CH_2); 2.03 (bm, 20H, CH_2)

^a Spectrum recorded on a Bruker WH 400 spectrometer, (CDCl₃, +20 °C). Other spectra run in CDCl₃ (+25 °C) on a Jeol FX60 spectrometer; b, broad; m, multiplet; q, quartet; s, singlet.

Table 4

¹³C NMR data for [MI₂(CO)(NCMe)($\eta^2, \eta^{2'}$ -1,8-CTDiyne)] and derivatives

Complex	¹³ C (δ , ppm)
1 ^a	207.48 (s, CO); 173.97 and 153.81 (s, $\text{C}\equiv\text{C}$); 111.60 (s, $\text{C}\equiv\text{N}$); 34.27, 32.77, 28.70, 26.19, 17.88 (m, CH_2); 6.77 (s, CH_3)
2 ^a	208.32 (s, CO); 169.03 and 142.55 (s, $\text{C}\equiv\text{C}$); 106.95 (s, <i>Me C</i> $\equiv\text{N}$); 29.62, 27.94, 23.70, 18.45 (m, CH_2); 5.62 (s, CH_3)
3 ^b	227.79 and 222.34 (s, $\text{C}\equiv\text{C}$); 209.50 (s, CO); 133.33, 130.86, 128.78, 127.35 (m, <i>Ph</i>); 78.54 and 75.48 (s, $\text{C}\equiv\text{C}$ free); 35.48, 28.72, 27.94, 16.64, 18.45 (m, CH_2)
4 ^c	210.83 (s, CO); 143.46 and 136.45 (s, $\text{C}\equiv\text{C}$); 120.72 (s, <i>CH</i>); 59.0 (s, CH_2O); 33.4, 30.67, 25.21, 24.3 (m, CH_2 and <i>Cy</i>); 15.07 (s, CH_3)
5 ^a	223.28 (s, $\text{C}\equiv\text{C}$); 120.27 (s, <i>CH</i>); 33.49, 33.17, 30.63, 27.69, 24.96 (m, CH_2 and <i>Cy</i>)
6 ^b	239.75 (s, $\text{C}\equiv\text{C}$); 212.72 (s, CO); 201.02 (s, CS_2); 80.82 (s, $\text{C}\equiv\text{C}$ free); 46.43, 44.63, 36.00 and 35.27 (s, CH_2N); 28.72–18.45 (m, CH_2); 12.99 and 12.51 (s, CH_3)
7 ^c	238.84 (s, $\text{C}\equiv\text{C}$); 215.06 (s, CO); 197.13 (s, CS_2); 80.56 (s, $\text{C}\equiv\text{C}$ free); 50.49, 44.38, 35.74 and 34.96 (s, CH_2N); 34.96–18.32 (m, CH_2)

^a Spectra recorded on a Bruker WH 400 spectrometer in CDCl₃ (+20 °C). ^b Spectra recorded on a Bruker WH-300 spectrometer in CDCl₃ (+20 °C). ^c Spectra recorded on a Jeol FX 60 spectrometer in CDCl₃ (+25 °C).

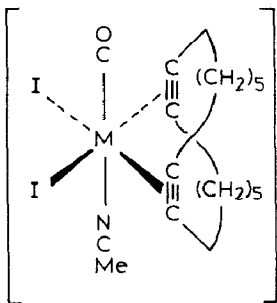


Fig. 1. Proposed structure of the complexes $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$.

alents of $\text{RC}_2\text{R}'$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$; for $\text{M} = \text{W}$ only, $\text{R} = \text{R}' = \text{Me}$, CH_2Cl and *p*-tol; $\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_2\text{OH}$) to give $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}')_2]$ which are all soluble in CH_2Cl_2 and CHCl_3 [15]. The lower solubility of $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ is probably due to the packing of the coordinated 1,8-CTDiyne giving strong forces between molecules in the lattice. In view of the similar colour and IR spectral properties of **1** and **2** to the complexes $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}')_2]$ ($\text{R} = \text{Me}$ and Ph), which have been structurally characterised by X-ray crystallography [15], it is highly likely that the structures of **1** and **2** will be similar. The proposed structures for **1** and **2** are shown in Fig. 1. The alkyne groups on the 1,8-CTDiyne ligand must also be *cis* with the alkyne groups parallel to each other with only five CH_2 groups between the alkyne ligands. Templeton and Ward [16] have correlated the number of electrons donated by the alkyne to the metal and the alkyne contact carbon chemical shifts. Since complexes **1** and **2** are only sparingly soluble in polar solvents the ^{13}C NMR spectra were measured on a 400 MHz instrument. The alkyne carbon contact shifts of **1** and **2** are at δ 173.97 and 153.81 ppm for **1** and δ 169.03 and 142.55 ppm for **2**. These values indicate that the alkynes are donating a total of six electrons to the metal in these complexes, i.e. an average of three from each alkyne. From these ^{13}C NMR spectra it is also highly unlikely that 1,8-CTDiyne is coordinated as a cyclobutadiene ligand in these complexes, as complexes such as $[\text{MI}_2(\text{CO})(\text{NCMe})(\eta^4\text{-1,8-CTDiyne})]$ would be "16-electron". The chemistry of **1** and **2** described below also confirms that the 1,8-CTDiyne ligand is bonded as a bisalkyne ligand in these complexes.

Reaction of the complexes **1** and **2** with phosphorus donor ligands is considerably slower than with the alkyne complexes $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R}')_2]$ ($\text{R} = \text{Me}$ or Ph). For example, **1** and **2** did not react with $\text{P}(\text{OMe})_3$ or PPh_3 even after refluxing in CHCl_3 for 24 h. However, reaction of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ with one equivalent $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppm) under reflux in CHCl_3 for 48 h gave the green complex $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-1,8-CTDiyne})]$, which is analogous to $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$. The X-ray crystal structure of $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$ has been determined [17], and the very similar colour and spectral properties of **3** indicate that the stereochemistry is likely to be very similar (Fig. 2). The ^{13}C NMR spectrum of 1,8-CTDiyne (+25°C, CDCl_3) shows an alkyne ($\text{C}\equiv\text{C}$) resonance at δ 80.83 ppm. Resonances at δ 78.54 and 75.48 ppm for **3** were observed which was expected since one alkyne ligand of the 1,8-CTDiyne is displaced by one phosphorus atom of the dppm leaving one "4-electron" alkyne coordinated to the tungsten. The very low field resonances at δ 227.79 and 222.34

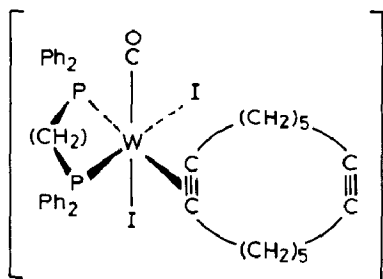


Fig. 2. Proposed structure of the complex $[WI_2(CO)(dppm)(\eta^2\text{-1,8-CTDiene})]$.

ppm are likely to be due to the alkyne donating "4-electrons" to the metal. However, without carrying out ^{13}C labelling studies it is difficult to distinguish between ^{13}C shifts of $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{O}$ in this type of complex, although it has often been found that the $\text{C}\equiv\text{C}$ resonances occur at lower field than the $\text{C}\equiv\text{O}$ resonances.

Complexes **1** and **2** also react with $\text{CyN}=\text{CHCH}=\text{NCy}$. The reaction of $[WI_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiene})]$ with one equivalent of $\text{CyN}=\text{CHCH}=\text{NCy}$ in CH_2Cl_2 at room temperature gives the cationic complex $[WI(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiene})]I \cdot \text{Et}_2\text{O}$ (**4**). The X-ray crystal structure of $[WI(\text{CO})(\text{bipy})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ is known [18], and since this complex has very similar physical and spectroscopic properties to **4** the structure shown in Fig. 3 is proposed for **4**. As expected the ^{13}C NMR spectrum of **4** shows alkyne contact carbons at δ 143.46 and 136.45 ppm which indicates that both alkynes are donating a total of six electrons to the metal, i.e. both alkyne groups of 1,8-CTDiene are coordinated in this complex. However, $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiene})]$ reacts with two equivalents of $\text{CyN}=\text{CHCH}=\text{NCy}$ to also give a monocationic non-carbonyl containing complex, $[\text{MoI}(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiene})]I$ (**5**). This is likely to be formed via the dicationic complex $[\text{Mo}(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiene})]^{2+}I$ which is analogous to $[\text{W}(\text{CO})(\text{bipy})_2(\eta^2\text{-PhC}_2\text{Ph})][\text{BPh}_4]_2$ [18]. ^1H and ^{13}C NMR data (see Tables 3 and 4) for **5** suggest that the two $\text{CyN}=\text{CHCH}=\text{NCy}$ ligands are in a similar environment, and hence the most likely structure for this complex has the alkyne *trans* to iodide as shown in Fig. 4. The ^{13}C NMR of **5** (see experimental) indicates that one alkyne is coordinated to the metal and one "free" in this complex.

Bisdithiocarbamate alkyne complexes of the type $[\text{M}(\text{CO})(\text{S}_2\text{CX})_2(\eta^2\text{-RC}_2\text{R}')]]$ have been extensively investigated [19–24]. The reactions of the tungsten complex

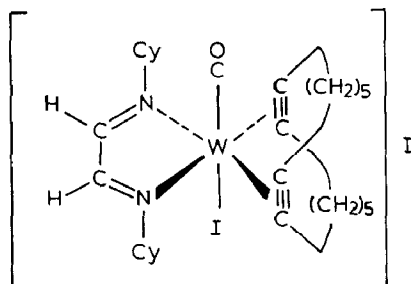


Fig. 3. Proposed structure of the complex $[WI(\text{CO})(\text{CyN}=\text{CHCH}=\text{NCy})(\eta^2, \eta^{2'}\text{-1,8-CTDiene})]I \cdot \text{Et}_2\text{O}$.

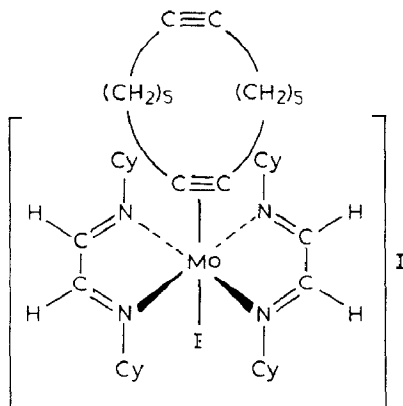


Fig. 4. Proposed structure of the complex $[\text{MoI}(\text{CyN}=\text{CHCH}=\text{NCy})_2(\eta^2\text{-1,8-CTDiyne})]\text{I}$.

$[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ with $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ and $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$ have been studied. IR studies indicate that reaction of **2** with one equivalent of either $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ or $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$ in CH_2Cl_2 gave a mixture of **2** and $[\text{W}(\text{CO})(\text{S}_2\text{CX})_2(\eta^2\text{-1,8-CTDiyne})]$ ($\text{X} = \text{NEt}_2$ and NC_4H_8). However, reaction of **2** with two equivalents of S_2CX^- ($\text{X} = \text{NEt}_2$ and NC_4H_8) gave the expected monoalkyne complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})_2(\eta^2\text{-1,8-CTDiyne})]$ (**6** and **7**). As has been previously observed for **3** and **5** from ^{13}C NMR spectroscopy, only one of the alkyne groups on 1,8-CTDiyne is coordinated to the tungsten. Since only two $\text{C}\equiv\text{C}$ resonances (coordinated and uncoordinated 1,8-CTDiyne) are observed for complexes **5**, **6** and **7** it is likely that rapid rotation of the 1,8-CTDiyne ligand is occurring (faster than the NMR timescale at room temperature) which has often been previously observed with monobut-2-yne complexes of molybdenum(II) and tungsten(II) [10,13,17].

Summarising these results it is evident that the special ability of molybdenum and tungsten to form coordinatively unsaturated bisalkyne and trisalkyne complexes has stabilised the formation of a macrocyclic diyne, such as 1,8-cyclotetradecadiyne, as a coordinated bisalkyne ligand in this system. The reactions of the bisalkyne complexes $[\text{Ml}_2(\text{CO})(\text{NCMe})(\eta^2, \eta^{2'}\text{-1,8-CTDiyne})]$ are similar to those of the other conventional bisalkyne compounds of the type $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ and Ph). However, they are slower, probably owing to the chelate effect of the macrocyclic diyne.

Experimental

All reactions were carried out under nitrogen by standard Schlenk line techniques. The complexes $[\text{Ml}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) were prepared by the published method [25], and all chemicals were purchased from commercial sources except $\text{CyN}=\text{CHCH}=\text{NCy}$ which was prepared by the literature method [26]. IR spectra were recorded as CHCl_3 films between NaCl plates on a Perkin-Elmer 197 IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX 60 MHz, a Bruker WH 300 MHz or a Bruker WH400 MHz NMR spectrometer (all spectra were calibrated against tetramethylsilane).

Preparation of [MoI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (1)

1,8-CTDiyne (0.365 g, 1.938 mmol) was added to a solution of [MoI₂(CO)₃(NCMe)₂] (1.000 g, 1.938 mmol) dissolved in CH₂Cl₂ (20 cm³). After 17 h stirring the orange precipitate was allowed to settle and the solvent syringed off. The precipitate was washed with 4 × 15 cm³ portions of CH₂Cl₂ and dried in vacuo. Yield 1.16 g, 99%.

In a similar reaction of [WI₂(CO)₃(NCMe)₂] with 1,8-CTDiyne gave a yellow precipitate of [WI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (2) (see Table 1 for yield and analytical data).

Reaction of 2 with Ph₂P(CH₂)PPh₂ (dppm)

To a stirred suspension of [WI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (0.300 g, 0.432 mmol) in CHCl₃ (30 cm³) was added dppm (0.166 g, 0.432 mmol). After 48 h refluxing, filtration and removal of solvent in vacuo gave bright green [WI₂(CO)(dppm)(η^2 -1,8-CTDiyne)], which was recrystallised from CH₂Cl₂. Yield 0.23 g, 57%.

Reaction of 2 with one equivalent of CyN=CHCH=NCy

To a stirred suspension of [WI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (0.400 g, 0.576 mmol) in CH₂Cl₂ (15 cm³) was added CyN=CHCH=NCy (0.127 g, 0.576 mmol). After 15 h, filtration and reduction of solvent in vacuo gave a dark brown solution, from which brown [WI(CO)(CyN=CHCH=NCy)(η^2, η'^2 -1,8-CTDiyne)]I · Et₂O (4) was precipitated with Et₂O. Cooling of a CH₂Cl₂/Et₂O solution of (4) to –30 °C produced brown crystalline aggregates of 4. Yield 0.39 g, 71%.

Reaction of 1 with two equivalents of CyN=CHCH=NCy

To [MoI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (0.500 g, 0.824 mmol) suspended in CH₂Cl₂ (15 cm³) was added CyN=CHCH=NCy (0.363 g, 1.647 mmol). After 17 h, filtration and removal of solvent in vacuo afforded [MoI(CyN=CHCH=NCy)₂(η^2 -1,8-CTDiyne)]I (5) as a brown crystalline powder, which was recrystallised from CH₂Cl₂/Et₂O. Yield 0.64 g, 79%.

Reaction of 2 with NaS₂CNEt₂ · 3H₂O

To [WI₂(CO)(NCMe)(η^2, η'^2 -1,8-CTDiyne)] (0.400 g, 0.576 mmol) in CH₂Cl₂ (15 cm³) was added NaS₂CNEt₂ · 3H₂O (0.259 g, 1.151 mmol). After 17 h filtration and removal of solvent in vacuo afforded [W(CO)(S₂CNEt₂)₂(η^2 -1,8-CTDiyne)] (6) as a dark green crystalline powder, which was recrystallised from CH₂Cl₂. Yield 0.17 g, 42%.

In a similar reaction of 2 with two equivalents of [NH₄][S₂CNC₄H₈] in CH₂Cl₂ gave the new complex [W(CO)(S₂CNC₄H₈)₂(η^2 -1,8-CTDiyne)] (7) (see Table 1 for colour and yield).

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