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2,2′:6′,2″-Terpyridine complexes of molybdenum(II) and tungsten(II). X-ray crystal structures of [MoI(CO)(terpy)(η^2-PhC_2Ph)]I and [WI(terpy)(η^2-PhC_2Ph)$_2$]I·$CDCl_3$

Nicholas Aimeloglou [a], Paul K. Baker [a,]*, Michael G.B. Drew [b], Bjoern Glaeser [a], Fiona Holland [a], Margaret M. Meehan [a]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK*

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Abstract

Equimolar quantities of [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) and terpy (terpy = 2,2′:6′,2″-terpyridine) react in CH_2Cl_2 at room temperature to give the cationic complexes [$MI(CO)_3$(terpy)]I (**1** and **2**) in high yield. Treatment of [$MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)$] with one equivalent of terpy affords [$Mo(GeCl_3)(CO)_2(PPh_3)$(terpy)]Cl (**3**) in good yield. Reaction of [MI_2(CO)(NCMe)(η^2-RC_2R)$_2$](M = Mo, W; R = Ph; for M = W only, R = Me) with an equimolar quantity of terpy in CH_2Cl_2 at room temperature gives the cationic complexes [MI(CO)(terpy)(η^2-RC_2R)]I (**4** and **5**) or the crystallographically characterised cationic complex [WI(terpy)(η^2-PhC_2Ph)$_2$]I (**6**). Equimolar quantities of [WI(CO)(terpy)(η^2-MeC_2Me)]I(**5**) and Na[BPh_4] react to give the anion-exchanged product, [WI(CO)(terpy)(η^2-MeC_2Me)][BPh_4] (**7**). The X-ray crystal structure of [MoI(CO)(terpy)(η^2-PhC_2Ph)]I shows the three nitrogen atoms of the terpy bonded in the equatorial plane of an octahedron together with the carbonyl group. The iodo and diphenylacetylene ligands are mutually *trans*- to each other in the axial positions. The structure of [WI(terpy)(η^2-PhC_2Ph)$_2$]I·$CDCl_3$ (**6**) has a distorted octahedral geometry, with the three nitrogen atoms of the terpy ligand in a *mer*-configuration, with two *cis*-and parallel diphenylacetylene ligands and an iodo group occupying the other three *mer*-sites. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Tungsten; Crystal structure; Terpyridine; Alkyne; Cationic complexes

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1. Introduction

Although there are many complexes of molybdenum and tungsten containing 2,2′-bipyridine ligands, very few molybdenum and tungsten complexes are known which contain 2,2′:6′,2″-terpyridine [1–8]. Two examples include the terpy complexes [$Mo(CO)_4$(terpy)] [9] and [Mo(terpy)$_2$] [10], with the terpy coordinated in bidentate and tridentate modes, respectively. Very recently, Daniel et al. [11] have described the synthesis of the seven-coordinate molybdenum(II) complexes [MoX(CO)(η^4-C_7H_8)(terpy)]X′ (X = Br, I; X′ = Br, I, PF_6, SbF_6), which has been crystallographically characterised for X = Br, X′ = SbF_6.

In 1986 [12], we described the synthesis of the new highly versatile seven-coordinate complexes, [$MI_2(CO)_3(NCMe)_2$] (M = Mo and W). In 1988, we described the reactions of [$WI_2(CO)_3(NCMe)_2$] with RC_2R (R = Me, Ph) to give the crystallographically characterised tungsten bis(alkyne) complexes [WI_2(CO)(NCMe)(η^2-RC_2R)$_2$] [13]. More recently, the related molybdenum complexes [MoI_2(CO)(NCMe)(η^2-RC_2R')$_2$] (R = R′ = Me or Ph; R = Me, R′ = Ph) [14] have been prepared.

The reactions of [MI_2(CO)(NCMe)(η^2-RC_2R)$_2$] (M = Mo and W) with 2,2′-bipyridine (bipy) are very different. For example, reaction of equimolar quantities

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* Corresponding author. Fax: +44-1248-370528.
E-mail address: chs018@bangor.ac.uk (P.K. Baker).

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Table 1
Physical and analytical data for complexes **1**–**7**

Complex	Colour	Yield (%)	Analytical data, found (Calc.) (%)		
			C	H	N
1 $[MoI(CO)_3(terpy)]I$	Black	68	32.3(32.4)	2.0(1.7)	6.6(6.3)
2 $[WI(CO)_3(terpy)]I$	Brown/Black	73	29.2(28.6)	1.6(1.5)	5.8(5.6)
3 $[Mo(GeCl_3)(CO)_2(PPh_3)(terpy)]Cl$	Purple/Black	53	49.0(48.8)	3.6(3.0)	5.4(4.9)
4 $[MoI(CO)(terpy)(\eta^2\text{-}PhC_2Ph)]I$	Brown	85	43.8(43.2)	2.5(2.4)	5.5(5.6)
5 $[WI(CO)(terpy)(\eta^2\text{-}MeC_2Me)]I$	Green	74	32.3(31.9)	2.3(2.3)	5.6(5.6)
6 $[WI(terpy)(\eta^2\text{-}PhC_2Ph)_2]I$	Brown/Orange	85	49.7(50.2)	3.3(3.0)	4.1(4.1)
7 $[WI(CO)(terpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Green	76	56.5(55.9)	3.9(3.8)	4.4(4.4)

of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and bipy in the presence of $Na[BPh_4]$ gives the crystallographically characterised complex $[WI(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]$-$[BPh_4]$ [15]. Whereas, a similar reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and bipy yields the neutral mono(2-butyne) complex $[MoI_2(CO)(bipy)(\eta^2\text{-}MeC_2Me)]$ [14]. In this paper, we describe the reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ and $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Me or Ph) with 2,2′:6′,2″-terpyridine. The molecular structures of the terpy complexes, $[MoI(CO)(terpy)(\eta^2\text{-}PhC_2Ph)]I$ and $[WI(terpy)(\eta^2\text{-}PhC_2Ph)_2]I\cdot CDCl_3$ are also discussed.

2. Results and discussion

2.1. Reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ with 2,2′:6′,2″-terpyridine

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and terpy react in CH_2Cl_2 at room temperature to give the cationic complexes $[MI(CO)_3(terpy)]I$ (**1**) and (**2**). A similar reaction of $[MoCl(GeCl_3)(CO)_3(NCMe)(PPh_3)]$ [16] with one equivalent of terpy gives $[Mo(GeCl_3)(CO)_2(PPh_3)(terpy)]Cl$ (**3**) in good yield. Complexes **1**–**3** were characterised by elemental analysis (C, H and N) (Table 1), IR and ^{1}H-NMR spectroscopy (Tables 2 and 3). Complexes **1**–**3** are only moderately soluble in CH_2Cl_2 and $CHCl_3$, and totally insoluble in diethyl ether and hydrocarbon solvents. The molybdenum $(GeCl_3)$ complex **3,** is less soluble than the iodo-complexes **1** and **2**. Complexes **1**–**3** are air-sensitive in solution, but can be stored under dinitrogen in the solid state for several days without decomposition. We have previously shown [17], that reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with equimolar amounts of PPh_3 give $[MI_2(CO)_3(NCMe)(PPh_3)]$, which react in situ with one equivalent of $N\hat{}N$ ($N\hat{}N$ = 2,2′-bipy or 1,10-phen) to give the cationic complexes, $[MI(CO)_3(PPh_3)(N\hat{}N)]I$. Hence, it is likely that the trinitrogen donor ligand, terpy displaces two acetonitrile ligands and an iodide from $[MI_2(CO)_3(NCMe)_2]$ to give the cationic seven-coordinate complexes, $[MI(CO)_3(terpy)]I$ (**1**) and (**2**). This was confirmed by the IR spectra (Table 2), which have three carbonyl bands in their spectra. In the complex $[Mo(GeCl_3)(CO)_2(PPh_3)(terpy)]Cl$ (**3**), the cationic formulation is confirmed by there being two carbonyl bands in its IR spectrum (Table 2) and elemental analysis results. Several unsuccessful attempts to grow suitable single crystals for X-ray analysis were made. The structures of halocarbonyl complexes of molybden-

Table 2
IR data (cm^{-1}) [a] for complexes **1**–**7**

Complex	$\nu(C{\equiv}O)$ (cm^{-1})	$\nu(C{\equiv}C)$ (cm^{-1})
(1)	2010(s), 1937(s), 1849(s)	–
(2)	1958(s), 1925(s), 1902(m)	–
(3)	1944(s), 1870(s)	–
(4)	1967(s)	1602(w)
(5)	1922(s)	1602(w)
(6)	–	1600(w)
(7)	1922(s)	1602(w)

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; m = medium, s = strong, w = weak.

Table 3
^{1}H-NMR data [a] for complexes **1**–**7**

Complex	^{1}H-NMR (δ) ppm
1	7.5 → 9.2 (m, terpy-*H*)
2	7.5 → 9.0 (m, terpy-*H*)
3	7.5 → 9.0 (m, 11H, terpy-*H*); 7.2 → 7.4 (m, 15H, *Ph*)
4	8.8 (m,2H,terpy-*N*-C*H*); 8.0 → 8.2 (m,4H,terpy-*H*), 7.3 → 7.5(m,15H,terpy-*H*, + *Ph*)
5	9.0 (d, 2H, terpy *N*-C*H*); 7.9 → 8.1(m, 4H, terpy-*H*); 7.5 (m, 5H, terpy-*H*); 3.0(s, 6H, C_2Me)
6	8.8 (m, 2H, terpy-*N*-C*H*), 8.0 → 8.2(m, 4H, terpy-*H*); 6.9 → 7.6(brm, 25H, terpy-*H* + *Ph*.)
7	7.5 → 9.1 (m,11H, terpy-*H*); 6.8 → 7.4 (m, 20H, BPh_4); 3.0(s, 6H, C_2Me)

[a] Spectra recorded in $CDCl_3$ (+25°C) referenced to $SiMe_4$.

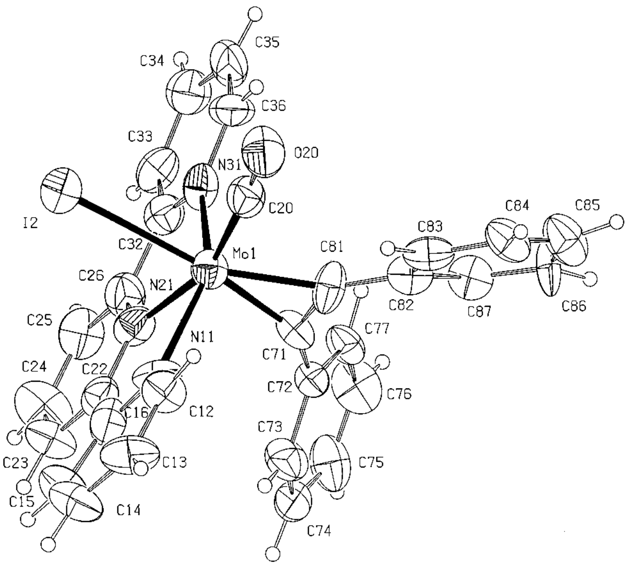

Fig. 1. The structure of the cation in (**4**), together with ellipsoids shown at 30% probability.

um(II) and tungsten(II) most commonly have capped octahedral geometry [18–22], which may be the geometry of complexes **1**–**3**.

2.2. Reactions of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ with 2,2′:6′,2″-terpyridine

Equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Ph; M = W only, R = Me) [13,14] and terpy react in CH_2Cl_2 at room temperature to give the cationic complexes $[MI(CO)(terpy)(\eta^2\text{-}RC_2R)]I$ (**4** and **5**), and the bis(alkyne) complex $[WI(terpy)(\eta^2\text{-}PhC_2Ph)_2]I$(**6**) in good yield. Complexes **4**–**6** have been characterised by elemental analysis (C, H and N) (Table 1), IR (Table 2) and ^{1}H-NMR spectroscopy (Table 3), and complexes **4** and **6** by X-ray crystallography. The cationic complexes **4**–**5** are soluble in polar chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but totally insoluble in diethyl ether, whereas the non-carbonyl containing cationic complex **6** is also soluble in CH_2Cl_2 and $CHCl_3$, but also slightly soluble in diethyl ether. Complexes **4**–**6** are all air-sensitive in solution, however they can all be stored under nitrogen in the solid state for several days without significant decomposition. The cationic nature of $[WI(CO)(terpy)(\eta^2\text{-}MeC_2Me)]I$ (**5**), was confirmed by the reaction of **5** with an equimolar amount of $Na[BPh_4]$ in acetonitrile to give the anion exchanged product, $[WI(CO)(terpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**7**), which has been fully characterised (see Tables 1–3). The cationic nature of these complexes was also confirmed by the X-ray crystal structure determinations of $[MoI(CO)(terpy)(\eta^2\text{-}PhC_2Ph)]I$ (**4**) and $[WI(terpy)(\eta^2\text{-}PhC_2Ph)_2]I{\cdot}CDCl_3$(**6**).

Suitable single crystals of $[MoI(CO)(terpy)(\eta^2\text{-}PhC_2Ph)]I$ (**4**) were grown from a concentrated $CDCl_3$ solution of **4** at room temperature. The structure of **4** is shown in Fig. 1, together with the atomic numbering scheme. The structure contains discrete $[MoI(CO)(terpy)(\eta^2\text{-}PhC_2Ph)]I$ cations and iodide anions. The cation is shown in Fig. 1 and selected bond lengths (Å) and angles (°) are presented in Table 4. The metal environment can best be considered as a distorted octahedron with the diphenylacetylene in an axial position occupying one site *trans* to the iodide. The terpy ligand is tridentate occupying the equatorial plane together with a carbonyl group. The dimensions from the metal atom are as expected; the bond to the central nitrogen, N(21) atom is at 2.10 (2) Å, shorter than the bonds to the two outer nitrogen atoms N(11) and N(31){2.23(2), 2.17(2) Å}, respectively. These distances are comparable with the values of 2.230 (4), 2.158(4) and 2.208 (5) Å found in $[MoBr(CO)(terpy)(\eta^4\text{-}C_7H_8)]^+$, [11]. Suitable single crystals of **6** were grown from a concentrated $CDCl_3$ solution of **6** in a NMR tube. The asymmetric unit of **6** consists of a discrete cation and anion together with a solvent deuterated chloroform molecule. The structure of the $[WI(terpy)(\eta^2\text{-}PhC_2Ph)_2]^+$ cation is shown in Fig. 2, together with the atomic numbering scheme, and the dimensions in the coordination sphere are given in Table 4. The environment of the metal coordination sphere can also be considered to be a distorted octahedron with the two PhC_2Ph ligands occupying single octahedral sites. The W–terpy distances are W–N(11){2.24(2)},W–N(21)-{2.21(3)}, W–N(31){2.37(3)} Å, with the central nitrogen *trans* to a PhC_2Ph ligand. The plane of the three-membered WCC ring makes an angle of 25.9° with the terpy ligand plane. The other PhC_2Ph ligand is *trans* to the iodide. There are very few examples of structures in the Cambridge Crystallographic Database containing the Mo(terpy) moiety, and indeed none containing the W(terpy) moiety. Of the structures containing the Mo(terpy) moiety, the only one related to the present structure is the aforementioned $[MoBr(CO)(terpy)(\eta^4\text{-}norbornadiene)][SbF_6]$ [11], where the carbonyl group is also *trans*-to the central nitrogen of the terpy in the equatorial plane and the bromide is *trans*- to the norbornadiene. There are related structures containing the bipyridyl ligand viz $[WI(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ [15], $[WCl(CO)(bipy)(\eta^2\text{-}MeC_2Me)_2]I$ [23], and where in both cations the equatorial plane is occupied by two mutually *cis* 2-butyne ligands, and the bipy ligand. Again the halides are *trans*- to the carbonyl groups.

In order to see if the complex, $[MoI(CO)(terpy\text{-}N,N')(\eta^2\text{-}PhC_2Ph)_2]I$, is initially formed which has terpy attached in a bidentate manner, the reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with one equivalent

Table 4
Selected bond lengths (Å) and angles (°) for **4**

Mo(1)–C(20)	1.98(2)
Mo(1)–C(71)	1.99(2)
Mo(1)–C(81)	2.04(2)
Mo(1)–N(21)	2.10(2)
Mo(1)–N(31)	2.17(2)
Mo(1)–N(11)	2.23(2)
Mo(1)–I(2)	2.873(3)
C(20)–Mo(1)–C(71)	115.2(8)
C(20)–Mo(1)–C(81)	77.7(8)
C(71)–Mo(1)–C(81)	37.6(7)
C(20)–Mo(1)–N(21)	160.7(7)
C(71)–Mo(1)–N(21)	83.8(7)
C(81)–Mo(1)–N(21)	121.3(7)
C(20)–Mo(1)–N(31)	102.2(7)
C(71)–Mo(1)–N(31)	88.4(6)
C(81)–Mo(1)–N(31)	97.7(7)
N(21)–Mo(1)–N(31)	73.8(6)
C(20)–Mo(1)–N(11)	104.5(7)
C(71)–Mo(1)–N(11)	97.9(6)
C(81)–Mo(1)–N(11)	107.2(8)
N(21)–Mo(1)–N(11)	74.4(6)
N(31)–Mo(1)–N(11)	146.6(6)
C(20)–Mo(1)–I(2)	78.2(6)
C(71)–Mo(1)–I(2)	165.6(5)
C(81)–Mo(1)–I(2)	155.6(6)
N(21)–Mo(1)–I(2)	82.6(4)
N(31)–Mo(1)–I(2)	83.4(4)
N(11)–Mo(1)–I(2)	82.8(4)

Selected bonds lengths (Å) and angles (°) for **6**

W(1)–C(61)	1.94(5)
W(1)–C(71)	2.08(5)
W(1)–C(91)	2.09(4)
W(1)–C(81)	2.09(3)
W(1)–N(21)	2.21(3)
W(1)–N(11)	2.24(2)
W(1)–N(31)	2.37(3)
W(1)–I(2)	2.888(4)
C(61)–W(1)–C(71)	32.3(16)
C(61)–W(1)–C(91)	87.6(18)
C(71)–W(1)–C(91)	106.4(17)
C(61)–W(1)–C(81)	95.1(15)
C(71)–W(1)–C(81)	95.4(13)
C(91)–W(1)–C(81)	35.1(12)
C(61)–W(1)–N(21)	164.8(15)
C(71)–W(1)–N(21)	162.1(15)
C(91)–W(1)–N(21)	86.4(13)
C(81)–W(1)–N(21)	88.0(9)
C(61)–W(1)–N(11)	93.3(15)
C(71)–W(1)–N(11)	119.9(14)
C(91)–W(1)–N(11)	86.4(12)
C(81)–W(1)–N(11)	120.1(9)
N(21)–W(1)–N(11)	72.4(9)
C(61)–W(1)–N(31)	122.2(16)
C(71)–W(1)–N(31)	90.4(15)
C(91)–W(1)–N(31)	111.4(13)
C(81)–W(1)–N(31)	78.5(9)
N(21)–W(1)–N(31)	73.0(9)
N(11)–W(1)–N(31)	139.7(9)
C(61)–W(1)–I(2)	99.1(14)
C(71)–W(1)–I(2)	87.2(12)
C(91)–W(1)–I(2)	162.7(10)
C(81)–W(1)–I(2)	156.8(7)
N(21)–W(1)–I(2)	83.0(7)
N(11)–W(1)–I(2)	77.4(7)
N(31)–W(1)–I(2)	78.5(6)

of terpy was followed by IR spectroscopy. Equimolar quantities of the complex, [MoI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] and terpy in CHCl$_3$ gave after 30 s an IR spectrum which showed all the [MoI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] {ν(CO) = 2080 cm^{-1}} had disappeared, and only a carbonyl band at 1967 cm^{-1}, due to the crystallographically characterised product, [MoI(CO)(terpy)-(η^2-PhC$_2$Ph)]I (**4**) was observed. Refluxing a CHCl$_3$ solution of **4** in the presence of dissolved PhC$_2$Ph for 12 h surprisingly did not give the carbonyl displaced product, [MoI(terpy)(η^2-PhC$_2$Ph)$_2$]I, related to the crystallographically characterised tungsten product, [WI(terpy)(η^2-PhC$_2$Ph)$_2$]I (**6**), which was the only product observed from the reaction of equimolar amounts of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] and terpy in CH$_2$Cl$_2$.

3. Conclusions

2,2′;6′,2″-Terpyridine(terpy) reacts with [MI$_2$(CO)$_3$-(NCMe)$_2$], [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(PPh$_3$)] and [MI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] to give a range of products, all of which have terpy coordinated in a tridentate manner. It is interesting to note that two different crystallographically characterised products, namely [MoI(CO)(terpy)(η^2-PhC$_2$Ph)]I (**4**) and [WI(terpy)(η^2-PhC$_2$Ph)$_2$]I (**6**) are obtained from reactions of equimolar amounts of [MI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] and terpy in CH$_2$Cl$_2$ at room temperature.

4. Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. All chemicals were purchased from commercial sources except for [MI$_2$(CO)$_3$(NCMe)$_2$] (M = Mo or W) [12], [MoCl(GeCl$_3$)(CO)$_3$(NCMe)(PPh$_3$)] [16], [MI$_2$(CO)-(NCMe)(η^2-RC$_2$R)$_2$] (M = Mo, W; R = Me, Ph) [13,14], which were prepared by the published methods.

Elemental analyses were determined using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer. The ^{1}H-NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer, and referenced to SiMe$_4$.

4.1. Preparation of [MoI(CO)$_3$(terpy)]I (1)

The complex [MoI$_2$(CO)$_3$(NCMe)$_2$] (0.305 g, 0.592 mmol) was dissolved in dry and degassed CH$_2$Cl$_2$ (30 cm^3) with continuous stirring under a stream of dry nitrogen and (0.138 g, 0.592 mmol) of terpy was added.

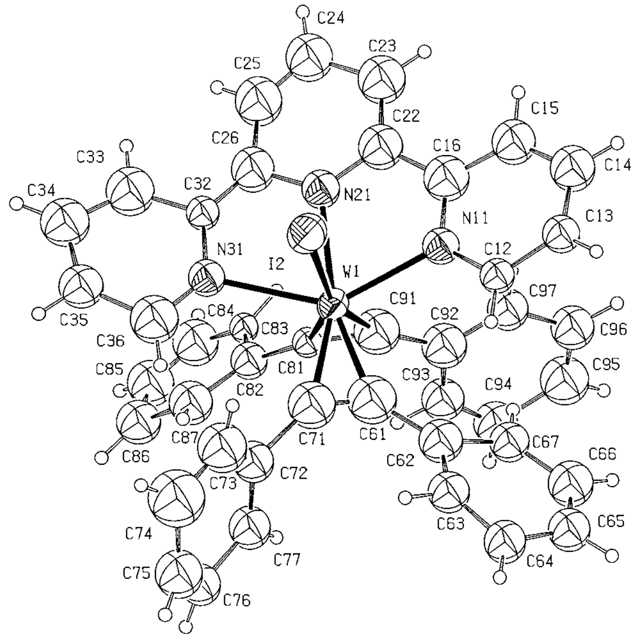

Fig. 2. X-ray crystal structure of the cation in (**6**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

After stirring for 2 h, the mixture was filtered and the solvent was removed in vacuo to give the black crystalline ionic solid, [MoI(CO)$_3$(terpy)]I (**1**), which was recrystallised from CH_2Cl_2 (yield = 0.268 g, 68%).

In similar reactions of equimolar quantities of [WI$_2$(CO)$_3$(NCMe)$_2$], [MoCl(GeCl$_3$)(CO)$_3$(NCMe)-(PPh$_3$)] and terpy gave the cationic complexes [WI(CO)$_3$(terpy)]I (**2**) and [Mo(GeCl$_3$)(CO)$_2$(PPh$_3$)-(terpy)]Cl (**3**), respectively. For physical and analytical data see Table 1.

*4.2. Preparation of [MoI(CO)(terpy)(η^2-PhC$_2$Ph)]I (**4**)*

To a solution of [MoI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (0.5 g, 0.06 mmol) in CH_2Cl_2 (30 cm^3), terpy (0.15g, 0.06 mmol) was added. After stirring for 17 h a green precipitate was allowed to settle, and the brown solution was removed by syringe and the solvent removed in vacuo to give the brown solid, [MoI(CO)(terpy)(η^2-PhC$_2$Ph)]I (**4**) which was recrystallised from $CHCl_3$ at − 17°C to give single crystals suitable for X-ray crystallography (yield = 0.41 g 85%).

In a similar reaction of equimolar quantities of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] and terpy in CH_2Cl_2 at room temperature (r.t.) gave [WI(CO)(terpy)(η^2-MeC$_2$Me)]I (**5**). For physical and analytical data see Table 1.

*4.3. Preparation of [WI(terpy)(η^2-PhC$_2$Ph)$_2$]I (**6**)*

To a solution of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (1.0 g, 1.15 mmol) in CH_2Cl_2 (30 cm^3) was added terpy (0.27 g, 1.15 mmol). After stirring at r.t., under an atmosphere of dry nitrogen for 24 h, followed by filtration and removal of the solvent in vacuo gave the brown–orange solid [WI(terpy)(η^2-PhC$_2$Ph)$_2$]I (**6**). The complex was recrystallised from CH_2Cl_2–Et_2O at − 17°C (yield = 1.02 g, 85%). Suitable single crystals for X-ray crystallography of **6** were grown from a concentrated $CDCl_3$ solution of **6** in a NMR tube.

4.4. Preparation of [WI(CO)(terpy)(η^2-MeC$_2$Me)] [BPh$_4$] (7)

To a solution of [WI(CO)(terpy)(η^2-MeC$_2$Me)]I (0.57 g,0.76 mmol) in NCMe (25 cm^3), Na[BPh$_4$](0.26 g, 0.76 mmol) was added. After stirring for 24 h followed by filtration and removal of the solvent in vacuo, the dark green powder was redissolved in CH_2Cl_2 (30 cm^3) and filtered, and the solvent removed in vacuo to give a dark green powder [WI(CO)(terpy)(η^2-MeC$_2$Me)] [BPh$_4$] (**7**) which was recrystallised twice from CH_2Cl_2 (yield = 0.54 g, 76%).

*4.5. Crystal structure and analysis of **4** and **6***

Crystal data for **4** and **6** are given in Table 5. Intensity data were collected with Mo–K$_\alpha$ radiation using the MARresearch Image Plate system. The crystals were positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [24].

The structures were solved using direct methods with the SHELX86 program [25]. In **4** all non-hydrogen atoms were refined with anisotropic thermal parameters. In **6** only the tungsten and iodine atoms were refined anisotropically. In both structures the hydrogen atoms were included in geometric positions and given thermal parameters equivalent at 1.2 times those of the atom to which they were attached. The data for **6** was of poor quality and constraints on thermal parameters for atoms in rings proved necessary. Empirical absorption corrections were carried out for both structures using the DIFABS program [26]. The structures were refined on F^2 using the SHELX program [27].

5. Supplementary material

For complexes **4** and **6**, tables of remaining molecular dimensions not included in this paper, anisotropic and isotropic thermal parameters, and hydrogen coordinates are available. Ordering information is given on any current masthead page. The data have been lodged with the Cambridge Crystallographic Database; CCDC nos. 142074 and 142075 for **4** and **6**, respectively. Copies of this information can be obtained free of

Table 5
Crystal data for **4** and **6**

Compound	**4**	**6**
Empirical formula	$C_{30}H_{20}I_2MoN_3O$	$C_{44}H_{32}C_{13}I_2N_3W$
Molecular weight	788.23	1146.72
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group, *Z*	$P2_1/n$, 4	$P\bar{1}$, 2
Unit cell dimensions		
a (Å)	14.356(12)	12.341(15)
b (Å)	11.684(12)	13.013(15)
c (Å)	17.149(17)	15.506(17)
α (°)	(90)	101.62(1)
β (°)	97.53(1)	111.86(1)
γ (°)	(90)	97.97(1)
V (Å^3)	2852	2200
D_{calc} (Mg m^{-3})	1.836	1.731
Absorption coefficient (mm^{-1})	2.652	4.243
F (000)	1508	1096
Crystal size (mm^3)	$0.35 \times 0.25 \times 0.20$	$0.25 \times 0.10 \times 0.10$
θ range for data collection (°)	2.40 to 25.03	2.46 to 25.93
Index ranges	$-17 \leq h \leq 17$ $0 \leq k \leq 13$ $-20 \leq l \leq 20$	$0 \leq h \leq 15$ $-16 \leq k \leq 15$ $-18 \leq l \leq 16$
Reflections measured	8035	7559
Independent reflections [R_{int}]	4663/0.0733	7559
Data/restraints/parameters	4663/0/335	7559/48/228
R indices ([$I > 2\sigma(I)$) R_1	0.1078	0.1215
wR_2	0.2358	0.2205
R indices (all data) R_1	0.2206	0.2643
wR_2	0.2882	0.2915
Largest difference peak and hole (e Å^{-3})	2.387, −0.770	1.594, −0.769

charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] P. Legzdins, J.C. Oxley, Inorg. Chem. 23 (1984) 1053.
[2] J.A. Connor, E.J. James, J. Organomet. Chem. 325 (1987) 181.
[3] J. Granifo, M.E. Vargas, J. Organomet. Chem. 408 (1991) 357.
[4] S. Stötzel, K. Wieghardt, B. Nuber, Inorg. Chem. 32 (1993) 2128.
[5] C.-H. Lai, C.-H. Cheng, W.-C. Chou, S.-L. Wang, Organometallics 12 (1993) 1105.
[6] M. Handa, M. Mikuriya, R. Nukada, H. Matsumoto, K. Kasuga, Bull. Chem. Soc. Jpn. 67 (1994) 3125.
[7] E.S. Dodsworth, A.A. Vlček, A.B.P. Lever, Inorg. Chem. 33 (1994) 1045.
[8] K. Shinozaki, Y. Kaizu, Bull. Chem. Soc. Jpn. 67 (1994) 2314.
[9] E.W. Abel, K.G. Orrell, A.G. Osborne, H.M. Pain, V. Šik, J. Chem. Soc. Dalton Trans. (1994) 111.
[10] H. Behrens, U. Anders, Z. Naturforsch. Teil B 19 (1964) 767.
[11] T. Daniel, H. Nagao, H. Nakajima, K. Tanaka, A. Nakamura, J. Organomet. Chem. 509 (1996) 225.
[12] P.K. Baker, S.G. Fraser, E.M. Keys, J. Organomet. Chem. 309 (1986) 319.
[13] E.M. Armstrong, P.K. Baker, M.G.B. Drew, Organometallics 7 (1988) 319.
[14] N. Aimeloglou, P.K. Baker, M.M. Meehan, M.G.B. Drew, Polyhedron 17 (1998) 3455.
[15] P.K. Baker, E.M. Armstrong, M.G.B. Drew, Inorg. Chem. 27 (1988) 2287.
[16] P.K. Baker, D. ap Kendrick, J. Organomet. Chem. 466 (1994) 139.
[17] P.K. Baker, M. Bamber, G.W. Rogers, J. Organomet. Chem. 367 (1989) 101.
[18] M.G.B. Drew, Prog. Inorg. Chem. 23 (1977) 67, and refs. cited therein.
[19] M. Melník, P. Sharrock, Coord. Chem. Rev. 65 (1985) 49, and refs. cited therein.
[20] C.W. Haigh, P.K. Baker, Polyhedron 13 (1994) 417.
[21] P.K. Baker, Adv. Organomet. Chem. 40 (1996) 45, and refs. cited therein.
[22] P.K. Baker, Chem. Soc. Rev. 27 (1998) 125, and refs. cited therein.
[23] P.K. Baker, M.G.B. Drew, M.M. Meehan, H.K. Patel, A. White, J. Chem. Res. (S) (1998) 379; J. Chem. Res. (M) (1998) 1461.
[24] W. Kabsch, J. Appl. Cryst. 21 (1988) 916.
[25] SHELX 86, G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467
[26] DIFABS, N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.
[27] SHELXL, G.M. Sheldrick, Program for crystal structure refinement. University of Göttingen, 1993.