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MONO AND BIMETALLIC COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II) CONTAINING 4,4'-DIPHENYLENECARBONITRILE

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The complexes $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ or W) react in CH_2Cl_2 at room temperature with two equivalents of 4,4'-diphenylenecarbonitrile (dpc) to afford the new seven-coordinate complexes, $[\text{M}_2(\text{CO})_3(4,4'\text{-dpc-}N)_2]$ (**1** and **2**) in good yield. Equimolar quantities of $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ and PPh_3 give $[\text{M}_2(\text{CO})_3(\text{NCMe})(\text{PPh}_3)]$, which react *in situ* with 4,4'-dpc to yield the mono-4,4'-diphenylenecarbonitrile complexes, $[\text{M}_2(\text{CO})_3(4,4'\text{-dpc-}N)(\text{PPh}_3)]$ (**3** and **4**). Treatment of the bis(alkyne) complexes, $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ and Ph) with one equivalent of 4,4'-dpc in CH_2Cl_2 at room temperature affords the acetonitrile displaced products, $[\text{W}_2(\text{CO})(4,4'\text{-dpc-}N)(\eta^2\text{-RC}_2\text{R})_2]$ (**5** and **6**). Reaction of equimolar quantities of $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ and **2** in CH_2Cl_2 at room temperature gives the 4,4'-dpc-bridged complex, $[\text{W}_2(\text{CO})\{\text{W}_2(\text{CO})_3(4,4'\text{-dpc-}N)(4,4'\text{-dpc-}N,N')\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**7**) in good yield. Similarly, equimolar amounts of $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ and Ph) and (**4**) react in CH_2Cl_2 to afford the bimetallic complexes, $[\text{W}_2(\text{CO})\{\text{W}_2(\text{CO})(4,4'\text{-dpc-}N,N')(\text{PPh}_3)\}(\eta^2\text{-RC}_2\text{R})_2]$ (**8** and **9**). The new bimetallic 4,4'-dpc-bridged alkyne complexes, $[\text{W}_2(\text{CO})\{\text{W}_2(\text{CO})(4,4'\text{-dpc-}N,N')(\eta^2\text{-MeC}_2\text{Me})_2\}(\eta^2\text{-MeC}_2\text{Me})_2]$ (**10**), $[\text{W}_2(\text{CO})\{\text{W}_2(\text{CO})(4,4'\text{-dpc-}N,N')(\eta^2\text{-PhC}_2\text{Ph})_2\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**11**) and $[\text{W}_2(\text{CO})\{\text{W}_2(\text{CO})(4,4'\text{-dpc-}N,N')(\eta^2\text{-MeC}_2\text{Me})_2\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**12**) are also described.

Keywords: Tungsten; Molybdenum; Carbonitrile; Synthesis

INTRODUCTION

The importance of seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) has been shown, for example, by Bencze and Kraut-Vass [1]. They showed that the complexes $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ and W ; $\text{X} = \text{Cl}$ and Br ; $\text{L} = \text{PPh}_3$ and AsPh_3) are active catalysts for the ring-opening polymerization of norbornene and norbornadiene. The rate determining step in these reactions [2] involves cleavage of the metal-phosphorus or arsine bond. More recently [3], we have made a preliminary study of the catalytic activity of the seven-coordinate bis(acetonitrile) complexes, $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$ and W), and their derivatives. Although a number of articles [4–17] have described monofunctional nitrile, seven-coordinate complexes of molybdenum(II) and tungsten(II), very few containing two nitrile functional groups

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have been published. One recent example from our own work [18] concerns the synthesis and characterization of a series of *o*-phenylenediacetonitrile seven-coordinate complexes, including the structurally characterized complex, $[\text{WI}_2(\text{CO})_3\{1,2\text{-C}_6\text{H}_4(\text{CH}_2\text{CN})_2\text{-}N\}_2]$, where the *o*-phenylenediacetonitrile is attached through one of the nitrile groups. In this article we describe the preparation and characterization of a series of 4,4'-diphenylenecarbonitrile mono- and bimetallic complexes of molybdenum(II) and tungsten(II).

EXPERIMENTAL

All reactions described were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo and W) [19] and $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) [20] were prepared by published methods. Dichloromethane was dried and distilled before use.

Elemental analyses (C, H and N) were determined using a Carlo Erba instrument, MOD 1108 (using helium as the carrier gas). IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. ^1H (referenced to SiMe_4) NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer. Molecular weights of selected complexes were determined by Rast's method [21], using camphor as standard.

$[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ (2)

To a stirred solution of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.200 g, 0.331 mmol) in degassed dichloromethane (20 cm^3) at room temperature was added 1,4-dpc (0.135 g, 0.662 mmol) and the solution was left to stir for one hour under a constant stream of nitrogen. The resulting solution was then filtered over Kieselguhr and the solvent removed *in vacuo* to give a brown powder, $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ (2), which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yield of pure product = 0.217 g, 71%.

A similar reaction of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ with two equivalents of 1,4-dpc in dichloromethane (20 cm^3) at room temperature gave $[\text{MoI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ (1) after recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. See Tables I–III for physical, analytical and spectroscopic data.

$[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ (4)

To a stirred solution of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.200 g, 0.331 mmol) in degassed dichloromethane (20 cm^3) at room temperature was added PPh_3 (0.087 g, 0.331 mmol). After one minute, 1,4-dpc (0.067 g, 0.331 mmol) was added, and the solution was left to stir for one hour under a constant stream of nitrogen. The resulting solution was filtered, and the solvent was removed *in vacuo* to give the yellow complex $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ (4), which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yield of pure product = 0.271 g, 83%.

A similar reaction of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ with one equivalent of PPh_3 , followed by addition of an equimolar amount of 1,4-dpc in CH_2Cl_2 at room temperature gave $[\text{MoI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ (3), which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$.

TABLE I Physical and analytical data for the 1,4-diphenylenedicarbonitrile complexes of molybdenum(II) and tungsten(II)

Complex	Colour	Yield %	Found (calcd.) %		
			C	H	N
(1) [MoI ₂ (CO) ₃ (1,4-dpc-N) ₂]	Black	60	44.5 (44.2)	2.1 (1.9)	7.1 (6.7)
(2) [Wl ₂ (CO) ₃ (1,4-dpc-N) ₂]	Brown	71	40.3 (40.0)	1.9 (1.7)	6.1 (6.0)
(3) [MoI ₂ (CO) ₃ (1,4-dpc-N)(PPh ₃)]	Red-brown	81	46.7 (46.7)	2.9 (2.6)	3.3 (3.1)
(4) [Wl ₂ (CO) ₃ (1,4-dpc-N)(PPh ₃)]	Yellow	83	43.3 (42.5)	2.2 (2.3)	2.6 (2.8)
(5) [Wl ₂ (CO)(1,4-dpc-N)- (η ² -MeC ₂ Me) ₂]	Yellow	63	35.8 (35.1)	2.9 (2.6)	3.1 (3.6)
(6) [Wl ₂ (CO)(1,4-dpc-N)- (η ² -PhC ₂ Ph) ₂]	Orange yellow	77	50.1 (50.3)	2.9 (2.8)	2.4 (2.7)
(7) [Wl ₂ (CO){Wl ₂ (CO) ₃ (1,4-dpc-N)- (1,4-dpc-N,N')}(η ² -PhC ₂ Ph) ₂]	Brown	64	41.6 (41.1)	2.4 (2.1)	2.8 (3.2)
(8) [Wl ₂ (CO){Wl ₂ (CO) ₃ - (1,4-dpc-N,N')(PPh ₃)}- (η ² -MeC ₂ Me) ₂]	Brown	59	36.1 (36.4)	2.9 (2.4)	1.6 (1.9)
(9) [Wl ₂ (CO){Wl ₂ (CO) ₃ - (1,4-dpc-N,N')(PPh ₃)}- (η ² -PhC ₂ Ph) ₂]	Brown	50	45.2 (45.2)	2.9 (2.6)	1.6 (1.7)
(10) [Wl ₂ (CO){Wl ₂ (CO)- (1,4-dpc-N,N')- (η ² -MeC ₂ Me) ₂ }(η ² -MeC ₂ Me) ₂]	Yellow	46	28.4 (28.7)	2.4 (2.4)	2.1 (2.1)
(11) [Wl ₂ (CO){Wl ₂ (CO)- (1,4-dpc-N,N')(η ² -PhC ₂ Ph) ₂ }- (η ² -PhC ₂ Ph) ₂]	Yellow	58	47.5 (46.8)	2.5 (2.6)	1.6 (1.5)
(12) [Wl ₂ (CO){Wl ₂ (CO)- (1,4-dpc-N,N')(η ² -MeC ₂ Me) ₂ }- (η ² -PhC ₂ Ph) ₂]	Yellow	72	43.0 (43.5)	3.1 (2.8)	2.1 (2.0)

TABLE II IR data^a for the 4,4'-diphenylenedicarbonitrile complexes of molybdenum(II) and tungsten(II)

Complex	ν(C≡O) cm ⁻¹	ν(N≡C) cm ⁻¹	ν(C≡C) cm ⁻¹
(1)	2034 (s) and 1966 (s, br)	2360 (w) and 2305 (w)	
(2)	2027 (s) and 1946 (s, br)	2355 (w) and 2304 (w)	
(3)	2037 (s) and 1979 (s, br)	2352 (w) and 2306 (w)	
(4)	2030 (s), 1960 (s) and 1912 (s)	2358 (w) and 2305 (w)	
(5)	2058 (s)	2357 (w) and 2306 (w)	1655 (w) and 1607 (w)
(6)	2082 (s)	2355 (w) and 2305 (w)	1654 (w) and 1603 (w)
(7)	2053 (s) and 2001 (br)	2355 (w) and 2305 (w)	1628 (w) and 1524 (w)
(8)	2030 (s) and 1965 (s)	2348 (w) and 2304 (w)	1657 (w) and 1604 (w)
(9)	2081 (br, s), 2067 (br, s) and 1911 (s)	2362 (w) and 2309 (w)	1642 (w) and 1561 (w)
(10)	2062 (br) and 1968 (s)	2361 (w) and 2305 (w)	1604 (w) and 1578 (w)
(11)	2080 (s, br) and 1972 (s)	2358 (w) and 2305 (w)	1654 (w) and 1577 (w)
(12)	2061 (s, br) and 1974 (s)	2361 (w) and 2305 (w)	1670 (w) and 1591 (w)

^aSpectra recorded as thin CHCl₃ films between NaCl plates; s = strong; br = broad; w = weak.

[Wl₂(CO)(1,4-dpc-N)(η²-MeC₂Me)₂] (5)

To a stirred solution of [Wl₂(CO)(NCMe)(η²-MeC₂Me)₂] (0.200 g, 0.325 mmol) in degassed CH₂Cl₂ (20 cm³) at room temperature was added 1,4-dpc (0.067 g, 0.325 mmol), and the solution was stirred for one hour. The mixture was then filtered, and the solvent removed *in vacuo* to give a yellow product, which was recrystallized from CH₂Cl₂/Et₂O (50 : 50 ratio), affording the analytically pure complex [Wl₂(CO)-(1,4-dpc)(η²-MeC₂Me)₂] (5) in good yield. Yield of product = 0.159 g, 63%.

TABLE III ^1H NMR data^a for the 4,4'-diphenylenedicarbonitrile complexes of molybdenum(II) and tungsten(II)

Complex	^1H NMR (δ) ppm
(1)	8.0 (d, 4H, H_A coord); 7.75 (d, 4H, H_D uncoord); 7.6 (d, 4H, H_B); 7.5 (d, 4H, H_C)
(2)	8.0 (d, 4H, H_A coord); 7.8 (d, 4H, H_D uncoord); 7.65 (d, 4H, H_B); 7.5 (d, 4H, H_C)
(3)	7.2–8.0 (br m, $Ph + C_6H_4CN$)
(4)	7.1–8.0 (br m, $Ph + C_6H_4CN$)
(5)	8.0 (d, 2H, H_A coord); 7.8 (d, 2H, H_D uncoord); 7.65 (d, 2H, H_B); 7.5 (d, 2H, H_C); 3.0 (s, 6H, $2 \times CCH_3$); 2.8 (s, 6H, $2 \times CCH_3$)
(6)	7.1–8.0 (br m, $Ph + C_6H_4CN$)
(7)	7.1–7.9 (br m, 36H, $Ph + C_6H_4CN$);
(8)	7.2–8.0 (br m, 23H, $Ph + C_6H_4CN$); 3.0 (s, 6H, $2 \times CCH_3$); 2.8 (s, 6H, $2 \times CCH_3$)
(9)	7.2–8.0 (br m, 43H, $Ph + C_6H_4CN$)
(10)	8.0 (d, 2H, H_A coord); 7.75 (d, 2H, H_D uncoord); 7.6 (d, 2H, H_B); 7.5 (d, 2H, H_C); 3.0 (s, 12H, $2 \times CCH_3$); 2.8 (s, 12H, $2 \times CCH_3$)
(11)	7.1–8.0 (br m, $Ph + C_6H_4CN$)
(12)	7.1–8.0 (br m, 28H, $Ph + C_6H_4CN$); 3.0 (s, 6H, $2 \times CCH_3$); 2.8 (s, 6H, $2 \times CCH_3$)

^aSpectra recorded in CDCl_3 (+25°C, referenced to SiMe_4); s = singlet; d = doublet; brm = broad multiplet.

A similar reaction between an equimolar amount of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ and 1,4-dpc in CH_2Cl_2 (20 cm^3) at room temperature affords the product $[\text{WI}_2(\text{CO})(1,4\text{-dpc-}N)(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**6**).

$[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N,N')(\text{PPh}_3)\}(\eta^2\text{-MeC}_2\text{Me})_2]$ (**8**)

To a stirred solution of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.100 g, 0.163 mmol) in degassed dichloromethane (20 cm^3) at room temperature was added $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ (0.161 g, 0.163 mmol). After stirring at room temperature for 24 h, the mixture was filtered and the solvent removed *in vacuo* to give a brown powder of $[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N,N')(\text{PPh}_3)\}(\eta^2\text{-MeC}_2\text{Me})_2]$ (**8**), which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (50:50 ratio). Yield of pure product = 0.139 g, 59%. Molecular weight [21] calculated for complex **8** = 1538; molecular weight found by Rast's method = 1391.

A similar reaction of equimolar amounts of $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ and $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ in CH_2Cl_2 (20 cm^3) at room temperature afforded the crystalline product, $[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(1,4\text{-dpc-}N,N')\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**7**). A similar reaction of equimolar quantities of $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ and $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ affords the bimetallic complex, $[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N,N')(\text{PPh}_3)\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (**9**).

$[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})(1,4\text{-dpc-}N,N')(\eta^2\text{-MeC}_2\text{Me})_2\}(\eta^2\text{-MeC}_2\text{Me})_2]$ (**10**)

To a stirred solution of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.100 g, 0.163 mmol) in degassed CH_2Cl_2 (20 cm^3) at room temperature was added $[\text{WI}_2(\text{CO})(1,4\text{-dpc-}N)(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.127 g, 0.163 mmol). After 24 h, the mixture was filtered and the solvent removed *in vacuo* to give a yellow powder of $[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})(1,4\text{-dpc-}N,N')(\eta^2\text{-MeC}_2\text{Me})_2\}(\eta^2\text{-MeC}_2\text{Me})_2]$ (**10**) which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$

(50:50 ratio). Yield of pure product = 0.101 g, 46%. Molecular weight calculated for complex **10** = 1302; molecular weight found by Rast's method [21] = 1420.

Similar reactions were carried out using equimolar amounts of $[\text{WI}_2(\text{CO})(\text{NCMe})-(\eta^2\text{-PhC}_2\text{Ph})_2]$ and $[\text{W}_2(\text{CO})(1,4\text{-dpc-}N)(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me, Ph) in degassed CH_2Cl_2 at room temperature to afford complexes (**11**) and (**12**).

RESULTS AND DISCUSSION

Reaction of $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo or W) with two equivalents of 4,4'-diphenylenedicarbonitrile(1,4-dpc) in CH_2Cl_2 at room temperature affords the new bis(nitrile) complexes $[\text{MI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ (**1** and **2**). The complexes were characterized by elemental analysis (C, H and N) (Table I), infrared spectroscopy (Table II) and ^1H NMR spectroscopy (Table III). The complexes are soluble in chlorinated solvents, but only sparingly soluble in diethylether. Both complexes are stable in the solid state when stored under nitrogen; however, they decompose rapidly in solution when exposed to air. The IR spectrum of (**1**) shows a carbonyl band at 2034 cm^{-1} , and a second broad peak corresponding to two *cis*-carbonyls at 1966 cm^{-1} , two nitrile peaks at 2360 and 2305 cm^{-1} , due to coordinated and uncoordinated nitriles, respectively. The IR spectrum of 1,4-dpc has nitrile bands at $\nu(\text{NC}) = 2358$ and 2306 cm^{-1} . The expected resonances for the phenyl protons of the complexes are clearly observable in the ^1H NMR spectrum. As IR spectra of (**1**) and (**2**) are similar to those of the bis(acetonitrile) complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo or W), and the structures of the bis(acetonitrile) complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo or W) have been determined [12], it is likely that the structures of the bis(4,4'-diphenylenedicarbonitrile) complexes $[\text{MI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ will be as shown in Fig. 1.

The complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})_2]$ (M = Mo or W) react with an equimolar quantity of PPh_3 in CH_2Cl_2 at room temperature to give the monoacetonitrile, seven-coordinate complexes $[\text{MI}_2(\text{CO})_3(\text{NCMe})(\text{PPh}_3)]$. These complexes react *in situ* with one equivalent of 1,4-dpc to afford, after one hour, the acetonitrile-displaced, mixed-ligand complexes, $[\text{MI}_2(\text{CO})_3(1,4\text{-dpc})(\text{PPh}_3)]$ (**3** and **4**) in 81 and 83% yields, respectively. The compounds were then characterized in the usual manner and results are recorded in Tables I–III. These mixed ligand complexes are more stable in air than the bis(nitrile) complexes (**1**) and (**2**), but they should be stored under an inert atmosphere of nitrogen for several days. They are not completely soluble in solvents such as CH_2Cl_2 or CHCl_3 , and even less so in diethylether.

The IR spectrum of $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(\text{PPh}_3)]$ (**4**) shows three strong carbonyl bands at 2030 , 1960 and 1912 cm^{-1} compared with only two peaks for the Mo analogue (**3**), showing carbonyl peaks at 2037 cm^{-1} and a broad peak at 1979 cm^{-1} for the *cis*-carbonyls. Again, the expected coordinated nitrile peaks appear at 2352 and 2306 cm^{-1} for complex (**3**), the uncoordinated nitrile at the lower wavenumber, and confirming the expected monodentate coordination of the ligand in these complexes. The structure of the complexes is likely to be of capped trigonal prismatic geometry, owing to the similarity of their spectroscopic data to those of previously described, mixed ligand, seven-coordinate structures, namely $[\text{WX}_2(\text{CO})_3(\text{NCMe})(\text{SbPh}_3)]$ (X = Br, I) [5]. Attempts were made to grow single crystals of complexes (**1** and **4**) for X-ray analysis from a cooled concentrated solution of $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$

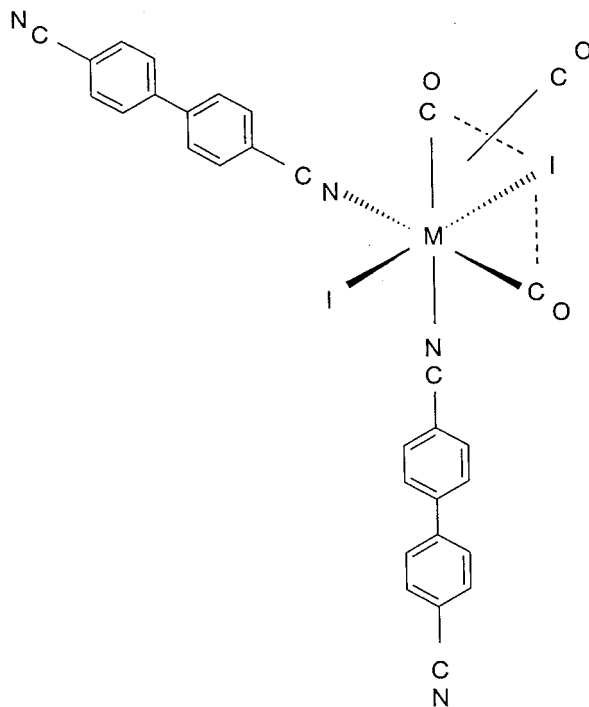


FIGURE 1 Proposed structure of $[\text{MI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ ($M = \text{Mo}$ and W) (1) and (2).

(50 : 50) mixture; however, no suitable crystals were obtained. A proposed structure of (3) and (4) is shown in Fig. 2.

The bis(alkyne) complexes $[\text{WI}_2(\text{CO})(1,4\text{-dpc-}N)(\eta^2\text{-RC}_2\text{R})_2]$ $\{\text{R} = \text{Me}$ (3), Ph (4) $\}$ were prepared by reacting equimolar quantities of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ or Ph) and 1,4-dpc in CH_2Cl_2 at room temperature for one hour. The complexes, once recrystallized, were characterized by elemental analysis, IR and ^1H NMR spectroscopy, and stored under nitrogen. The complexes are very unstable in solution and decompose rapidly when exposed to air. The IR spectrum (CHCl_3) of (5) shows a single strong carbonyl band at 2058 cm^{-1} , and bands at 2357 and 2306 cm^{-1} due to coordinated and uncoordinated nitrile bands of the ligand. As expected, the carbonyl band at $\nu(\text{CO}) = 2058\text{ cm}^{-1}$ is at slightly higher frequency than its acetonitrile analogue $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ [20], which has $\nu(\text{CO}) = 2050\text{ cm}^{-1}$ in the same solvent. Bands are also present due to alkyne stretches at 1655 and 1607 cm^{-1} . The ^1H NMR spectrum shows the expected resonances for the nitrile ligand and additional resonances at 2.8 and 3.0 ppm for the alkyne protons for complex (5). As expected, the ^1H NMR spectrum of complex (6) shows a large broad multiplet at $7.1\text{--}7.8\text{ ppm}$, due to the presence of the phenyl protons. In view of the similarity of the infrared data of these two bis(alkyne) complexes already characterized by X-ray crystallography [20], the most likely structure of (5) and (6) is shown in Fig. 3.

Reaction of $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ with one equivalent of $[\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)_2]$ (2) in CH_2Cl_2 at room temperature affords the acetonitrile-displaced bimetallic complex, $[\text{WI}_2(\text{CO})\{\text{WI}_2(\text{CO})_3(1,4\text{-dpc-}N)(1,4\text{-dpc-}N,N')\}(\eta^2\text{-PhC}_2\text{Ph})_2]$ (7) in 64%

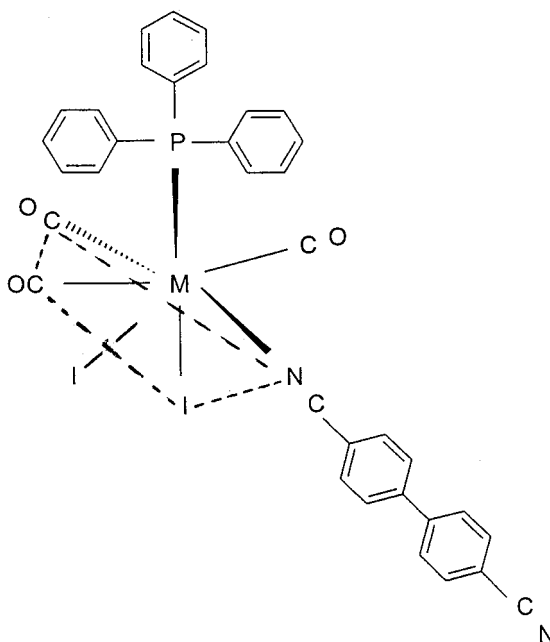


FIGURE 2 Proposed structure of $[MI_2(CO)_3(1,4\text{-dpc-}N)(PPh_3)]$ ($M = Mo$ and W) (3) and (4).

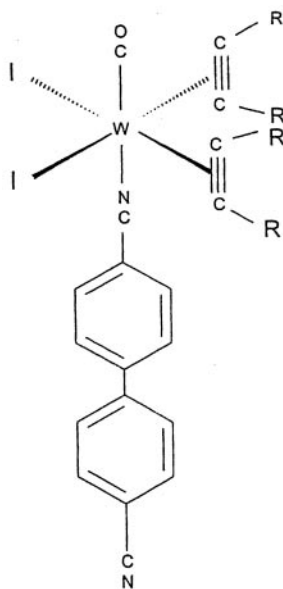


FIGURE 3 Proposed structure of $[WI_2(CO)(1,4\text{-dpc-}N)(\eta^2\text{-RC}_2\text{R})_2]$ ($R = Me$ or Ph) (5) and (6).

yield. A similar reaction of $[WI_2(CO)_3(1,4\text{-dpc-}N)(PPh_3)]$ (4) with $[WI_2(CO)(NCMe)(\eta^2\text{-RC}_2\text{R})_2]$ ($R = Me$ or Ph) in CH_2Cl_2 at room temperature affords the complexes $[WI_2(CO)\{WI_2(CO)_3(1,4\text{-dpc-}N,N')(PPh_3)\}(\eta^2\text{-RC}_2\text{R})_2]$ [$R = Me$ (8); $R = Ph$ (9)]. The products were characterized in the usual manner and physical and analytical data is

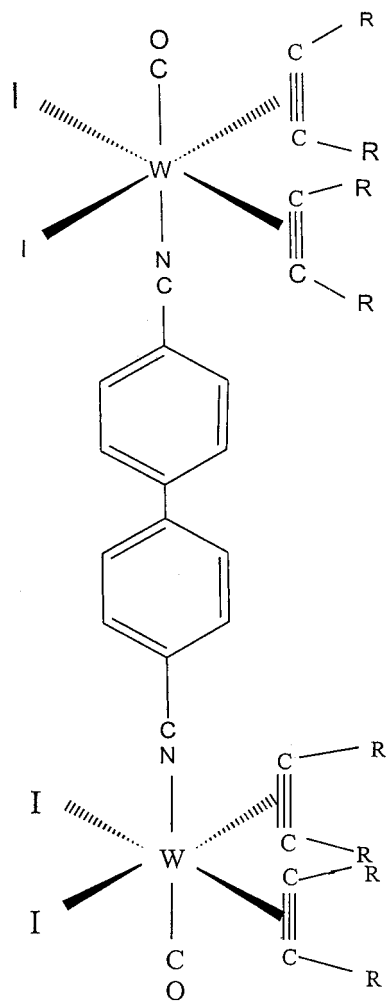


FIGURE 4 Proposed structure of $[\text{Wl}_2(\text{CO})\{\text{Wl}_2(\text{CO})(1,4\text{-dpc-}N,N')(\eta^2\text{-RC}_2\text{R})_2\}(\eta^2\text{-RC}_2\text{R})_2]$ (**10-12**).

detailed in the tables. The complexes are air-sensitive, and need to be stored under a dinitrogen atmosphere. The solubilities of these new bimetallic complexes proved to be very poor compared to the monometallic complexes prepared earlier (**1-6**), even in chlorinated solvents such as CH_2Cl_2 and CHCl_3 , and this posed some problems in obtaining high quality ^1H NMR spectra. IR spectra show varying trends for the carbonyl peaks of these new bimetallic complexes. The IR spectrum of (**9**) shows three main carbonyl bands, a strong band at 2081 cm^{-1} corresponding to the carbonyl group in $[\text{Wl}_2(\text{CO})(L')(\eta^2\text{-RC}_2\text{R})_2]$ ($(L' = \mathbf{4})$ $\{v(\text{CO})$ of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ is 2090 cm^{-1} } [20] while the carbonyl bands in L' can be assigned to the peaks at 2067 and 1911 cm^{-1} (broad and strong).

Three new bimetallic complexes were prepared by reacting equimolar quantities of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ or Ph) and (**5** or **6**) to form $[\text{Wl}_2(\text{CO})\{\text{Wl}_2(\text{CO})(1,4\text{-dpc-}N,N')(\eta^2\text{-RC}_2\text{R})_2\}(\eta^2\text{-RC}_2\text{R})_2]$ ($\text{R} = \text{Me}$ or Ph) (**10-12**). Again, these reactions took 24 h to complete and were carried out in CH_2Cl_2 at room

temperature. The complexes were characterized in the usual manner and physical and analytical data are reported in the tables. All complexes are, as expected, yellow, the same color as that of the starting reagents $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$.

These new bimetallic complexes (**10–12**) are air-sensitive, and hence should be stored under nitrogen. In solution they readily decompose on being exposed to air. The complexes are less stable than the monometallic complexes (**1–6**), and the previous bis(alkyne) bimetallic complexes (**7–9**). IR spectra of complexes (**10–12**) each show a strong band for the carbonyl in the unit $[\text{WI}_2(\text{CO})\text{L}'(\eta^2\text{-RC}_2\text{R})_2]$, at 2062 cm^{-1} (**10**), 2080 cm^{-1} (**11**) and 2061 cm^{-1} (**12**). ^1H NMR spectra (**10**) clearly shows features for both sets of alkyne methyl protons at 2.8 and 3.0 ppm. The other two complexes (**11**) and (**12**) both contain phenyl alkyne protons which appear as a broad multiplets and obscure the protons on the bis(nitrile) donor ligand. Many alkyne complexes of this type have been characterized by X-ray crystallography and a proposed structure of complexes (**10–12**) is shown in Fig. 4. The molecular weight of **11** has been determined by Rast's method [21] and gives an indication of the bimetallic nature of these complexes.

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