REACTIONS OF $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) WITH 1,4-DIAZA-1,3-BUTADIENES

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Abstract—Reaction of $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) in CH₂Cl₂ at room temperature with an equimolar quantity of R'N : CHCH : NR' (R' = Cy, 'Pr, Ph, *p*-MePh or *p*-MeOPh) gave high yields of the new cationic bisalkyne complexes [WI(CO)(R'N :CHCH : NR')(η^2 -RC₂R)₂]I via successive displacement of acetonitrile and an iodide ligand. The cationic compounds $[WI(CO)(CyN : CHCH : NCy)(\eta^2-RC_2R)_2][BPh_4]$ were also prepared by reaction of $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ with CyN : CHCH : NCy in the presence of Na[BPh_4] in order to confirm the ionic nature of these complexes. ¹³C NMR spectroscopy indicated that the two alkyne ligands are donating a total of six electrons to the metal in these complexes.

Cationic alkyne complexes of molybdenum(II) and tungsten(II) have proved to be important in recent years mainly due to the susceptibility of the coordinated alkyne ligand to nucleophilic attack.¹ Some examples of cationic alkyne complexes of molybdenum(II) and tungsten(II) are: $[Mo(CO)(\eta^2 RC_2R'_2(\eta^5-C_5H_5)$ [BF₄] (R = R' = Me or Ph, R = H, R' = Me; R = H, R' = Bu';² [M(CO)(η^2 - $MeC_2Me_2(\eta^{5}-C_5H_5)][PF_6]$ (M = Mo W):³ or $[Mo(CO)L(\eta^2-RC_2R')(\eta^5-C_5H_5)][BF_4]$ (L = CO, $P(OPh)_3$, PEt_3 or PPh_3 ; R = R' = H, Me or Ph; R = H; R' = Ph);⁴ [MoLL'(η^2 -RC₂R')(η^5 -C₅H₅ or $\eta^{5}-C_{9}H_{7}$][BF₄] (L,L' = CO and PR₃; L = L' = P(OMe)₃; R,R' = Me, Ph etc.);⁵ [MoI(CNR)₄(η^2 - $Bu'NHC_2NHBu'$]I (R = Me or Bu').⁶ Hitherto, there have been no examples of cationic alkyne complexes of molybdenum(II) or tungsten(II) containing 1,4-diaza-1,3-butadienes as attached ligands. Hence in this paper we wish to report the synthesis and spectral properties of some new cationic bisalkyne complexes [WI(CO)(R'N: CHCH: NR') $(\eta^2$ -RC₂R)₂]I (R = Me or Ph; R' = Cy, ^{*i*}Pr, Ph, *p*-MePh or *p*-MeOPh) and [WI(CO) $(CyN: CHCH: NCy)(\eta^2 - RC_2R)_2$ [BPh₄].

EXPERIMENTAL

All preparations were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. CH_2Cl_2 was dried over P_4O_{10} and distilled before use.

The complexes $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) were prepared by literature methods⁷ and the ligands R'N:CHCH:NR' (R' = Cy, ⁱPr, Ph, *p*-MePh or *p*-MeOPh) were also prepared by standard literature methods.⁸⁻¹² [W(CO)₆], RC₂R etc were all purchased from commercial sources.

¹H and ¹³C NMR spectra were recorded on either a Jeol FX 60 MHz spectrometer or a Bruker WH-400 MHz spectrometer (all spectra were calibrated against tetramethylsilane). IR spectra were recorded on a Perkin–Elmer 197 IR spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas).

$[WI(CO)(CyN:CHCH:NCy)(\eta^2-MeC_2Me)_2]I (1)$

To $[WI_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ (0.500 g, 0.813 mmol) dissolved in CH₂Cl₂ (15 cm³) with continuous stirring under a stream of dry nitrogen was

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added CyN: CHCH: NCy (0.179 g, 0.813 mmol). After stirring for 17 h, filtration, removal of the solvent *in vacuo* gave dark red crystals of [WI(CO) (CyN: CHCH: NCy)(η^2 -MeC₂Me)₂]I (yield = 0.57 g, 88%), which were recrystallized from CH₂Cl₂/Et₂O.

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2 - RC_2R)_2]$ (R = Me or Ph) with R'N: CHCH: NR' (R' = Cy, 'Pr, Ph, *p*-MePh or *p*-MeOPh) afford the new complexes $[WI(CO)(R'N: CHCH: NR')(\eta^2 - RC_2R)_2]I$ (**2–10**). (See Table 1 for colours and yields.)

$[WI(CO)(CyN:CHCH:NCy)(\eta^2-MeC_2Me)_2][BPh_4] \cdot \frac{1}{2}CH_2Cl_2(11)$

To $[WI_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ (0.500 g, 0.813 mmol), dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry nitrogen was added CyN: CHCH: NCy (0.179 g, 0.813 mmol) followed by Na[BPh₄] (0.278 g, 0.813 mmol) and the mixture was stirred for 17 h. Filtration, to remove NaI and removal of the solvent *in vacuo* gave brown crystals of [WI(CO)(CyN: CHCH: NCy) $(\eta^2-MeC_2Me)_2$][BPh₄] $\cdot \frac{1}{2}$ CH₂Cl₂ (yield = 0.64 g, 76%), which were recrystallized from CH₂Cl₂/Et₂O.

In a similar reaction of $[WI_2(CO)(NCMe)(\eta^2 - PhC_2Ph)_2]$ with CyN:CHCH:NCy followed by

Na[BPh₄] gave the new compound [WI(CO) (CyN: CHCH: NCy)(η^2 -PhC₂Ph)₂][BPh₄] (12). (See Table 1 for colour and yield.)

RESULTS AND DISCUSSION

Equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2 RC_2R_2$] (R = Me or Ph) and R'N: CHCH: NR' react in CH₂Cl₂ at room temperature to give high yields of the new cationic bisalkyne complexes $[WI(CO)(R'N: CHCH: NR')(\eta^2-RC_2R)_2]I.$ Reaction of $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ with CyN : CHCH: NCy in CH₂Cl₂ followed by Na[BPh₄] in a 1:1:1 molar ratio gave after filtration good yields of $[WI(CO)(CyN : CHCH : NCy)(\eta^2 - RC_2R)_2][BPh_4].$ All the new complexes (1-12) described in this paper have been fully characterized by elemental analysis (C, H and N) (Table 1), IR (Table 2), and ¹H and ¹³C NMR spectroscopy (Tables 3 and 4). Complexes (3, 8 and 11) are either CH_2Cl_2 or $\frac{1}{2}$ CH₂Cl₂ solvates which were confirmed by repeated elemental analyses and ¹H NMR spectroscopy. The complexes are soluble in polar solvents such as CH₂Cl₂ and CHCl₃, and as expected, since the complexes are cationic they are insoluble in diethylether and hydrocarbon solvents. The complexes are all moderately stable in the solid state

	Complex	Colour	Yield %	С	Н	Ν
(1)	$[WI(CO)(Cydab)(\eta^2-MeC_2Me)_2]I$	dark red	88	35.2	4.7	3.4
				(34.8)	(4.6)	(3.5)
(2)	$[WI(CO)(Cydab)(\eta^2-PhC_2Ph)_2]I$	dark green	80	49.7	4.5	2.3
				(49.5)	(4.3)	(2.7)
(3)	$[WI(CO)(^{i}Prdab)(\eta^{2}-MeC_{2}Me)_{2}]I \cdot CH_{2}Cl_{2}$	dark red	64	26.8	3.7	3.3
				(27.1)	(3.8)	(3.5)
(4)	$[WI(CO)(^{i}Prdab)(\eta^{2}-PhC_{2}Ph)_{2}]I$	dark green	69	45.8	4.0	2.7
				(46.2)	(3.8)	(2.9)
(5)	$[WI(CO)(MePhdab)(\eta^2-MeC_2Me)_2]I$	dark red	80	37.6	3.7	3.1
				(37.1)	(3.5)	(3.5)
(6)	[WI(CO)(MePhdab)(η^2 -PhC ₂ Ph) ₂]I	dark green	70	51.5	3.8	2.6
				(51.1)	(3.4)	(2.7)
(7)	$[WI(CO)(Phdab)(\eta^2-MeC_2Me)_2]I$	brown	75	35.3	3.0	3.4
				(35.3)	(3.1)	(3.6)
(8)	$[WI(CO)(Phdab)(\eta^2 - PhC_2Ph)_2]I \cdot \frac{1}{2}CH_2Cl_2$	brown	71	48.7	3.3	2.4
				(48.7)	(3.1)	(2.6)
(9)	$[WI(CO)(MeOPhdab)(\eta^2-MeC_2Me)_2]I$	red-brown	72	35.4	3.6	2.9
				(35.7)	(3.4)	(3.3)
(10)	$[WI(CO)(MeOPhdab)(\eta^2-PhC_2Ph)_2]I$	brown	84	49.8	3.7	2.3
				(49.6)	(3.3)	(2.6)
(11)	$[WI(CO)(Cydab)(\eta^2 - MeC_2Me)_2][BPh_4] \cdot \frac{1}{2}CH_2Cl_2$	brown	76	54.9	5.9	2.9
	_			(55.4)	(5.6)	(2.7)
(12)	$[WI(CO)(Cydab)(\eta^2-PhC_2Ph)_2][BPh_4]$	dark green	78	64.9	5.3	2.3
				(65.2)	(5.2)	(2.3)

Table 1. Physical and analytical^{*a*} data for the complexes [WI(CO)(Rdab)(η^2 -RC₂R)₂][X]

^a Calculated values in parentheses.

	νCO	vC≡=C
Complex	(cm ⁻¹)	(cm ⁻¹)
(1)	2052(s)	1648(vw)
(2)	2090(s)	1660(vw)
(3)	2060(s)	1640(vw)
(4)	2095(s)	1640(vw)
(5)	2050(s)	1690(w)
(6)	2090(s)	1695(w)
(7)	2047(s)	1692(vw)
(8)	2085(s)	1660(vw)
(9)	2050(s)	1652(vw)
(10)	2095(s)	1650(vw)
(11)	2052(s)	1638(vw)
(12)	2087(s)	1650(vw)

Table 2. IR data^{*a*} for the complexes $[WI(CO)(Rdab)(\eta^2-RC_2R)_2][X]$

^{*a*} Spectra recorded as CHCl₃ films between NaCl plates.

and can be stored under nitrogen for several weeks in the dark.

The reaction of the complexes $[WI_2(CO)(NCMe)(\eta^2 - RC_2R)_2]$ with an equimolar amount of R'N: CHCH: NR' probably proceeds via an initial displacement of an acetonitrile ligand since the reactions of $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) with one equivalent of pyridine (L) give $[WI_2(CO)L(\eta^2-RC_2R)_2]^{13}$ This is followed by displacement of iodide by the other nitrogen atom to give the observed products. It is interesting to note that the reaction of $[WI_2(CO)(NCMe)(\eta^2 RC_2R_2$] with bidentate phosphine ligands (LL) the neutral mono-alkyne complexes gives $[WI_2(CO)(LL)(\eta^2 - RC_2R)]^{14}$ with no evidence for the formation of any cationic intermediates. DAB's (1,4-diaza-1,3-butadienes) are poorer π acceptor and better σ -donor ligands than phosphines and hence these more electron-rich ligands can stabilize the formation of the cationic bisalkyne complexes.

Since the X-ray crystal structure of the closely related 2,2'-bipyridyl(bipy) complex [WI(CO)(bipy) $(\eta^2-MeC_2Me)_2$][BPh₄] has been determined¹³ and has very similar spectroscopic properties to the DAB complexes (1)–(12), the structures of the bisalkyne complexes (1)–(12) are likely to be very similar (Fig. 1).

The IR spectra of the complexes (1)–(12) all show a single carbonyl band in the IR spectrum well above 2000 cm⁻¹. Since the tungsten(II) complexes are cationic and have two alkyne ligands which are competing for electron density to back-bond into their π^* -orbitals there is little electron density available on the metal for back donation to the π^* -

Table 3. ¹H NMR spectra^{*a*} for the complexes [WI(CO) (Rdab)(η^2 -RC₂R)₂][X]

Complex	$^{1}\mathrm{H}\left(\delta ight)$ ppm				
(1) ^b	8.74 (s, 2H, CH); 3.32 (d, 6H, MeC ₂); 2.98 (d, 6H, MeC ₂); 1.78, 1.71, 1.69, 1.57, 1.21, 1.12, 1.09 (brm, 22H, Cy).				
(2) ^{<i>b</i>}	8.3 (s, 2H, CH); 7.54, 7.52, 7.36, 7.35, 7.33, 7.30 (brm, 20H, <i>Ph</i>); 2.0, 1.78, 1.2 (brm, 22H, <i>Cy</i>).				
(3)	8.85 (s, 2H, CH); 7.78, 7.51 (d, 2H, CH(Me) ₂), 5.3 (s, 2H, CH ₂ Cl ₂); 3.37 (s, 6H, MeC ₂); 3.06 (s, 6H, MeC ₂); 1.42, 1.37, 1.21 (t, 12H,. Me).				
(4) ^b	8.36 (s, 6H, C <i>H</i>); 7.57 (s, 2H, C <i>H</i> ,(Me) ₂); 7.54, 7.52, 7.36, 7.33 (brm, 20H, <i>Ph</i> C ₂); 1.65, 1.63 (d, 6H, <i>Me</i>); 1.54, 1.52 (d, 6H, <i>Me</i>).				
(5) ^{<i>b</i>}	7.64 (s, 2H, CH); 7.35, 7.25 (brm, 8H, Ph); 2.98 (s, 12H, MeC ₂); 2.35, 2.16 (d, 6H, MePh).				
(6) ^b	7.84, 7.82 (d, 2H, CH); 7.55, 7.53, 7.47, 7.41, 7.38 (brm, 20H, PhC ₂ and 8H, Ph); 2.30, 1.99 (d, 6H, MePh).				
(7) ^{<i>b</i>}	7.49 (s, 2H, C <i>H</i>); 7.25 (brm, 10H, <i>Ph</i>); 3.22, 2.98 (d, 12H, <i>Me</i> C ₂).				
(8)	7.81 (s, 2H, CH); 7.4, 7.22 (brm, 20H, PhC_2 and 10H, Ph); 5.26 (s, 1H, CH ₂ Cl ₂).				
(9) ^b	8.23 (s, 2H, CH); 7.76, 7.74, 7.69, 7.53 (brm, 8H, Ph); 3.83, 3.79 (d, MeO); 2.98 (s, 12H, MeC ₂).				
(10) ^b	8.31 (s, 2H, C <i>H</i>); 7.54, 7.52, 7.42, 7.35, 7.33 (brm, 20H, <i>Ph</i> C ₂ and 8H, <i>Ph</i>); 3.87, 3.8 (m, 6H, <i>Me</i> O).				
(11)	7.78 (s, 2H, C <i>H</i>); 7.49, 7.01, 6.9 (brm, 20H, <i>Ph</i>), 5.17 (s, 1H, CH ₂ Cl ₂); 3.24 (s, 6H, <i>Me</i> C ₂); 2.8 (s, 6H, <i>Me</i> C ₂); 1.74, 1.20 (brm, 22H, <i>Cy</i>).				
(12)	8.32 (bs, 2H, CH); 7.54, 7.01 (brm, 40H, PhC_2 and Ph); 1.93, 1.43 (brm, 22H, Cy).				
^{<i>a</i>} Spectra run in CDCl ₃ (+25°C) referenced to Me ₄ Si. ^{<i>b</i>} Spectra run on a Bruker WH 400.					
	$\begin{bmatrix} C \\ C \\ C \\ C \\ R \\ C \\ R \end{bmatrix}$				
	Г к]				

Fig. 1. Proposed structure of $[WI(CO)(R'N:CHCH: NR')(\eta^2-RC_2R)_2]^+$

Table 4. Selected ¹³C NMR spectra^{*a*} for the complexes $[WI(CO)(Rdab)(\eta^2-RC_2R)_2][X]$

Complex	13 C (δ) ppm
(1) ^b	203.18 (s, CO); 172.06, 161.91 (s, C=C); 161.8, 120.0 (s, CH); 34.05, 30.61, 25.42, 25.06, 24.57, 24.23, 23.43 (brm, CH_2); 16.99 (s, MeC_2).
(2) ^b	188.61, 162.27 (s, $C \equiv C$); 143.6, 142.0 (s, CH); 136.98, 136.47, 131.34, 128.88, 128.08, 127.99, 127.85, 127.11 (brm, <i>Ph</i>); 35.61, 33.64, 33.51, 30.77, 25.77, 25.1, 24.56 (brm, CH_2).
(3)	203.76 (s, CO); 172.18, 162.05 (s, $C \equiv C$); 143.2, 120.2 (s, CH); 61.99 (s, CH(Me) ₂); 52.11 (s, CH ₂ Cl ₂); 23.78 (s, Me); 19.88, 17.57 (s, MeC ₂).
(4) ^b	188.70, 141.81 (s, $C \equiv C$); 139.88 (s, CH); 131.27, 128.90, 128.02, 127.93, 127.07 (m, <i>Ph</i>); 89.01 (s, $CH(Me)_2$); 23.02, 20.97 (s, <i>Me</i>).
(6) ^b	208.00 (s, CO); 188.60, 156.40 (s, C=C); 144.80, 139.90 (s, CH); 136.85, 131.25, 129.88, 129.52, 128.49, 128.0, 127.91 (brm, Ph), 20.89 (s, Me).
(7)*	208.15 (s, <i>CO</i>); 198.15, 158.8 (s, <i>C</i> ≡ <i>C</i>); 151.64 (s, <i>CH</i>); 134.0, 130.9, 129.37 (brm, <i>Ph</i>); 29.5, 18.9 (s, <i>Me</i> C ₂).
(8) ^b	222.6 (s, CO), 174.78, 163.86 (s, $C \equiv C$); 137.23, 135.4 (s, CH); 131.51, 129.82, 128.78, 128.52, 128.0, 127.73 (brm, Ph); 52.1 (s, CH_2Cl_2).
(9) ^b	192.6, 161.01 (s, $C \equiv C$); 151.6, 140.51 (s, CH); 136.93, 127.86, 126.91, 125.45, 123.71 (brm, Ph); 29.39 (s, Me); 18.85 (s, MeC_2).
(10) ^{<i>b</i>}	208.03 (s, CO); 161.16 (s, C≡C); 136.9 (s, CH); 131.32, 128.53, 128.07, 127.98 (brm, PH); 29.40 (s, Me).
^a Spectra	run in CDCl ₃ (+25°C) referenced to Me ₄ Si.

^b Spectra run on a Bruker WH 400.

Carbonyl carbon is not seen in some of spectra as no relaxing agent $Cr(acac)_3$ was added to the solutions.

orbitals of the carbon monoxide ligand. The ¹H NMR spectra all show resonances expected for the static structures shown in Fig. 1. The ¹³C NMR spectra of (1)–(12) all show resonances in the range 198.15–141.81 ppm for the alkyne contact carbon atoms. Templeton and Ward¹⁵ have shown how ¹³C NMR chemical shifts of coordinated alkynes can be related to the number of electrons donated to the metal centre. The range of values from 198.15

to 141.81 ppm in these complexes indicate that the alkyne ligands are donating an average of "three electrons" each to the tungsten atom. However it is highly likely that one alkyne ligand is donating four electrons and the other two electrons with rapid equilibration of these hybrids occurring (faster than the NMR time scale).

The complexes [WI(CO)(CyN:CHCH:NCy) $(\eta^2-RC_2R)_2$]I were refluxed in CHCl₃ for 8 h in an attempt to afford the neutral "four electron" alkyne complexes [WI₂(CO)(CyN:CHCH:NCy) (η^2-RC_2R)] analogous to the bidentate phosphine compounds [WI₂(CO)(LL)(η^2-RC_2R)]¹⁴ without success. Also the complex [WI(CO) (CyN:CHCH:NCy)(η^2-MeC_2Me)₂]I does not appear to react with P(OMe)₃ even after refluxing in CHCl₃ for 24 h.

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