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Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with t-butylisonitrile

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Abstract

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) react with one, two, three, four, or five equivalents of CN^tBu in CH_2Cl_2 at room temperature to give $[WI_2(CO)(CN^tBu)(\eta^2\text{-}RC_2R)_2]$ (**1** and **2**), $[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}RC_2R)]$ (**3** and **4**), $[WI_2(CN^tBu)_3(\eta^2\text{-}RC_2R)]$ (**5** and **6**), $[WI(CN^tBu)_4(\eta^2\text{-}RC_2R)]I$ (**7** and **8**), $[W(CN^tBu)_5(\eta^2\text{-}RC_2R)]2I$ (**9** and **10**) respectively. The ^1H NMR data are used to indicate the likely stereochemistry of **1–10**, and the ^{13}C NMR spectra to indicate the number of electrons donated by the alkyne ligands to the tungsten in selected compounds.

Introduction

During the past 30 years four-electron donor alkyne complexes of molybdenum and tungsten have received considerable attention. A recent extensive review by Templeton described "four-electron alkyne ligands in molybdenum(II) and tungsten(II) complexes" [1]. A number of reports have been published concerning alkyne complexes of molybdenum(II) and tungsten(II) that also contain attached isonitrile ligands [2–15]. We describe here the reactions of one, two, three, four, and five equivalents of CN^tBu with $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph).

Results and discussion

The starting materials for this research, $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) were prepared by reaction of RC_2R with $[WI_2(CO)_3(NCMe)_2]$ in CH_2Cl_2 solution at 0°C [16]. The bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) react with one, two, three, four, or five equivalents of CN^tBu in CH_2Cl_2 at room temperature to afford the complexes $[WI_2(CO)(CN^tBu)(\eta^2\text{-}$

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Table 1

Physical and analytical data for the CN^tBu alkyne complexes of tungsten(II)

Complex	Colour	Yield (% of pure product)	Analysis (Found (calc.) (%))		
			C	H	N
$[WI_2(CO)(CN^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**1**)	Pale green	51	25.6	3.4	2.2
			(25 6)	(3.2)	(2.1)
$[WI_2(CO)(CN^tBu)(\eta^2\text{-}PhC_2Ph)_2]$ (**2**)	Green	78	45.1	3.2	1.6
			(45 0)	(3.4)	(1.5)
$[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}MeC_2Me)]$ (**3**)	Dark green	57	26.6	3.9	3.6
			(26.3)	(3.5)	(4.1)
$[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}PhC_2Ph)]$ (**4**)	Green	65	38 2	3.5	3.5
			(37 0)	(3.5)	(3.5)
$[WI_2(CN^tBu)_3(\eta^2\text{-}MeC_2Me)]$ (**5**)	Dark blue/green	70	31 0	4.6	5.7
			(30.8)	(4.5)	(5.6)
$[WI_2(CN^tBu)_3(\eta^2\text{-}PhC_2Ph)]$ (**6**)	Green	60	40 3	4.3	4.9
			(40.6)	(4.8)	(5.1)
$[WI(CN^tBu)_4(\eta^2\text{-}MeC_2Me)]I$ (**7**)	Dark green	66	34.8	5.2	6.3
			(35.0)	(5.1)	(6 8)
$[WI(CN^tBu)_4(\eta^2\text{-}PhC_2Ph)]I$ (**8**)	Green	67	43 1	4 9	5.9
			(43 0)	(4.8)	(5.5)
$[W(CN^tBu)_5(\eta^2\text{-}MeC_2Me)]2I$ (**9**)	Dark green	72	38 0	5.4	7.3
			(38 4)	(5.7)	(7 7)
$[W(CN^tBu)_5(\eta^2\text{-}PhC_2Ph)]2I$ (**10**)	Dark green	70	45 4	5.4	6.8
			(45 1)	(4.7)	(6.5)

$RC_2R)_2]$ (**1** and **2**), $[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}RC_2R)]$ (**3** and **4**), $[WI_2(CN^tBu)_3(\eta^2\text{-}RC_2R)]$ (**5** and **6**), $[WI(CN^tBu)_4(\eta^2\text{-}RC_2R)]I$ (**7** and **8**), and $[W(CN^tBu)_5(\eta^2\text{-}RC_2R)]2I$ (**9** and **10**), respectively. The complexes **1–10** have been characterised by elemental analysis (C, H and N) (Table 1) and by IR (Table 2) and by ^1H, and in selected cases, ^{13}C NMR spectroscopy (Tables 3 and 4). As expected, complexes **1–10** are all soluble in CH_2Cl_2 and $CHCl_3$; the but-2-yne complexes are more soluble than their diphenylacetylene counterparts. They become increasingly more soluble with successive introduction of further CN^tBu ligands. The cationic com-

Table 2

IR spectral data [a] for the CN^tBu alkyne complexes of tungsten(II)

Complex	$\nu(C{=}N)$	$\nu(C{\equiv}O)$
1	2195m	2089s
2	2180s	2000s
3	2150vs, 2180s	2060s
4	2160s, 2200s	2000s
5	2180w, 2150vs	–
6	2180s, 2150s	–
7	2170w, 2145vs	–
8	2180w, 2150s	–
9	2175w, 2148vs	–
10	2175w, 2150s	–

[a] Spectra recorded as thin films in $CHCl_3$ between NaCl plates (in cm^{-1}). w = weak; m = medium; s = strong; vs = very strong.

Table 3

^{1}H NMR data ^{a} for the CN^tBu alkyne complexes of tungsten(II)

Complex	$\delta(^1H)$ (ppm)
1	2.90, 2.92 (s, 12H, C_2*Me*); 1.41 (s, 9H, *Me*)
2	7.44 (m, 20H, Ph-*H*); 1.3 (s, 9H, *Me*)
3	3.14 (s, 6H, C_2*Me*); 1.83 (s, 9H, *Me*); 1.36 (s, 9H, *Me*)
4	7.5 (m, 10H, Ph-*H*); 1 51 (s, 9H, *Me*); 1.35 (s, 9H, *Me*)
5	3.15 (s, 3H, C_2*Me*); 2.83 (s, 3H, C_2*Me*); 1.85 (s, 9H, *Me*); 1.61 (s, 18H, *Me*)
6	7.35 (m, 10H, Ph-*H*); 1.5 (s, 9H, *Me*), 1.34 (s, 18H, *Me*)
7	3.14 (s, 3H, C_2*Me*); 2.79 (s, 3H, C_2*Me*); 1.59 (s, 36H, *Me*)
8	7.36 (m, 10H, Ph-*H*); 1.35 (s, 36H, *Me*)
9	3.14 (s, 3H, C_2*Me*); 2.93 (s, 3H, C_2*Me*); 1.59 (brs, 9H, *Me*); 1.38 (brs, 36H, *Me*)
10	7.4 (m, 10H, Ph-*H*); 1.54 (brs, 9H, *Me*); 1.32 (brs, 36H, *Me*)

^{a} Spectra recorded in $CDCl_3$ (+25°C) and referenced to Me_4Si; s = singlet; d = doublet; b = broad; brs = broad singlet; m = multiplet.

plexes **7–10** are insoluble in hydrocarbon solvents and diethyl ether. All the complexes are moderately air-sensitive but can be stored under nitrogen in Schlenk tubes for several days.

The reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with an equimolar amount of CN^tBu with displacement of acetonitrile to give $[WI_2(CO)(CN^tBu)(\eta^2\text{-}RC_2R)_2]$ are likely to occur by an associative mechanism since alkyne ligands can rearrange their mode of bonding from that of a four-electron donor to that of a two-electron donor in the transition state. Other workers [17,18] have suggested associative mechanisms for reactions of donor ligands with alkyne complexes of molybdenum(II) and tungsten(II). The ^{13}C NMR spectrum of **1** shows two but-2-yne contact carbon resonances at $\delta = 160.1$ and 154.6 ppm. According to Templeton and Ward's [19] correlation between the number of electrons donated by an alkyne and its ^{13}C NMR alkyne contact carbon chemical shift, the but-2-yne ligands in **1** are donating a total of six electrons to the tungsten centre. The structure of complexes **1** and **2** are likely to have the isonitrile ligand *trans-* to carbon monoxide, with the two *cis-* and parallel alkyne ligands as shown in Fig. 1. The crystal structures of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph) [16], and $[WI_2(CO)\{NCCH_2(3\text{-}C_3H_4S)\}(\eta^2\text{-}MeC_2Me)_2]$ [20] have been determined and exhibit this geometry. Furthermore the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with CO gave the acetonitrile displaced product $[WI_2(CO)_2(\eta^2\text{-}$

Table 4

Selected ^{13}C NMR data ^{a} for the CN^tBu alkyne complexes of tungsten(II)

Complex	$\delta(^{13}C)$ (ppm)
1	204 6 (s, *C*≡O); 160.1, 154.6 (s, *C*≡*C*); 163.8 (s, *C*=N); 58.7 (s, *C*Me$_3$); 30.4 (s, *Me*); 19.0, 18.7 (s, C_2*Me*)
4	209.0 (s, *C*≡*C*); 208 0 (s, *C*≡O); 204.6 (s, *C*≡*C*); 171 5 (d, C=N); 129.7–127.7 (m, Ph); 58.8 (s, *C*Me$_3$); 57.7 (s, *C*Me$_3$); 28.8 (s, *Me*); 28.2 (s, *Me*)
5	233.1 (s, *C*≡*C*); 222.0 (s, *C*≡*C*); 163.5 (s, *C*=N); 142.1 (s, *C*=N); 58 4, 57.6 (s, *C*Me$_3$); 30.3, 30.2 (s, *Me*); 18.7 (brs, *Me*C_2)

^{a} Spectra recorded in $CDCl_3$ (+25°C) and referenced to Me_4Si.

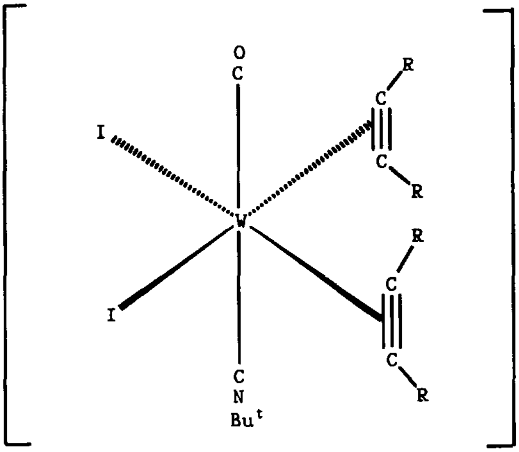

Fig. 1. Proposed structure for $[WI_2(CO)(CN^tBu)(\eta^2-RC_2R)_2]$ (1 and 2).

$MeC_2Me)_2]$ which was shown by X-ray crystallography [21] to have a *trans*-dicarbonyl structure.

Two equivalents of CN^tBu react with $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) to give, by replacement of both an acetonitrile and an alkyne ligand, the mono(alkyne) complexes $[WI_2(CO)(CN^tBu)_2(\eta^2-RC_2R)]$ (**3** and **4**). Since the ^1H NMR spectra of **3** and **4** show the presence of inequivalent CN^tBu ligands, it is very likely the two CN^tBu ligands will be *cis*- to each other, as shown in Fig. 2 (i and ii). Theoretical calculations [22,23] suggest that for a four-electron alkyne donor ligand the CO and RC_2R ligands must be *cis*-, with the (C≡C) bond parallel to the M–CO bond. Since many X-ray crystal structures [16,20,21,24–27] of halo-alkyne complexes have the alkyne ligand *trans*- to a halide, the most likely structure for **3** and **4** is that shown in Fig. 2(i). Attempts to grow single crystals for X-ray analysis in order to try and confirm the suggested structure for **3** and **4** were unsuccessful.

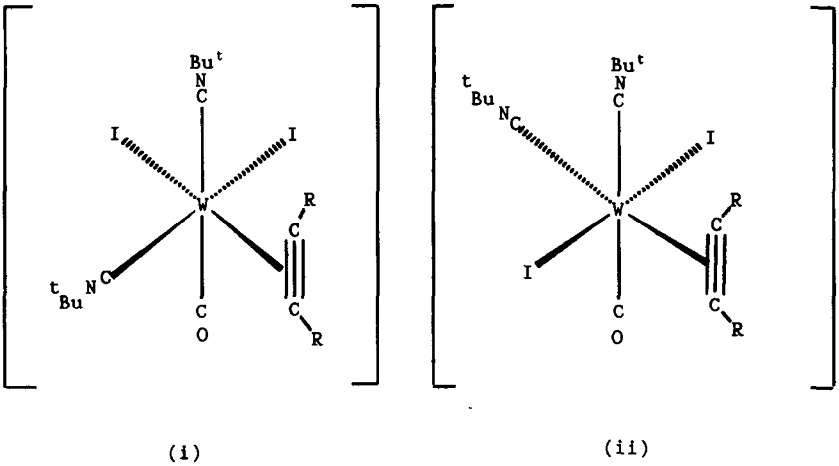

Fig. 2. Possible structures for $[WI_2(CO)(CN^tBu)_2(\eta^2-RC_2R)]$ (3 and 4).

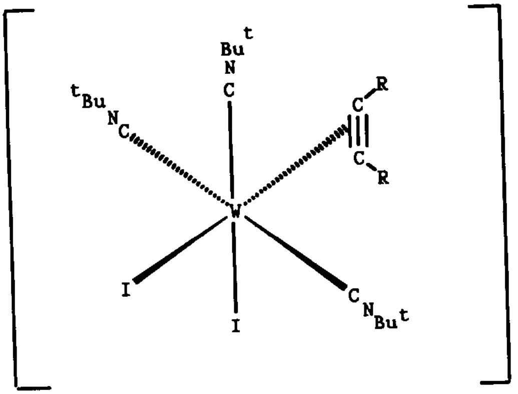

Fig. 3. Most likely structure for $[WI_2(CN^tBu)_3(\eta^2\text{-}RC_2R)]$ (5 and 6).

Reaction of three equivalents of CN^tBu with $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ affords the non-carbonyl containing products $[WI_2(CN^tBu)_3(\eta^2\text{-}RC_2R)]$ (**5** and **6**). Since the ^1H NMR spectra of, for example **5** shows two different ^tBu resonances at $\delta = 1.61$ and 1.85 ppm with an intensity ratio of 2/1, and again assuming the more likely structure with a halo group *trans*- to an alkyne, the most probable structure for **5** and **6** is shown in Fig. 3. The ^{13}C NMR spectrum of **5** shows two equal intensity alkyne (C≡C) resonances at $\delta = 233.1$ and 222.0 ppm which indicates [19] that the diphenylacetylene ligand in this complex is donating four electrons to the tungsten in this complex.

Four equivalents of CN^tBu react with $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) to give the cationic four-electron alkyne complexes $[WI(CN^tBu)_4(\eta^2\text{-}RC_2R)]I$ (**7** and **8**). The related molybdenum(II) complexes $[MoX(CNR)_4(\eta^2\text{-}RNHC_2NHR)]X$ have been prepared by the reductive coupling of two isonitrile ligands on the seven-coordinate complexes $[MoI(CNR)_6]X$ [2–8]. The crystal structures of the molybdenum(II) alkyne complexes $[MoX(CN^tBu)_4(\eta^2\text{-}{}^tBuHNC_2NH^tBu)]X'$ ($X = I$, $X' = PF_6$; $X = Br$, $X' = \frac{1}{2}ZnBr_4$; $X = CN$, $X' = PF_6$) have been determined and shows a capped trigonal prismatic structure [3]. It is

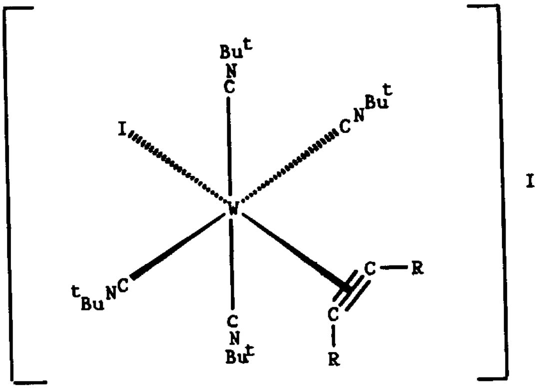

Fig. 4. Proposed structure for $[WI(CN^tBu)_4(\eta^2\text{-}RC_2R)]I$ (7 and 8).

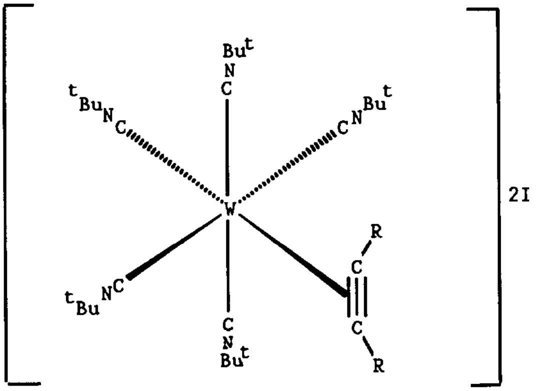

Fig. 5. Proposed structure of $[W(CN^tBu)_5(\eta^2\text{-}RC_2R)]2I$ (**9** and **10**).

very likely the structure of the tungsten(II) alkyne complexes **7** and **8** is similar as shown in Fig. 4.

The reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with five equivalents of CN^tBu gave the dicationic four-electron alkyne complexes $[W(CN^tBu)_5(\eta^2\text{-}RC_2R)]2I$ (**9** and **10**). The complexes **9** and **10** are related to the complex $[Mo(CN^tBu)_5(\eta^2\text{-}{}^tBuNHC_2NH^tBu)][NO_3]_2$ reported by Lippard and co-workers [8], and their structure of which is likely to be the one shown in Fig. 5. However, the X-ray crystal structure of the 2,2′-bipyridine derivative $[Mo(CN^tBu)_3(bipy)(\eta^2\text{-}{}^tBuNHC_2NH^tBu)][NO_3]_2$ has been determined [8] and has a pentagonal bipyramidal geometry.

Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with six and seven equivalents of CN^tBu were attempted in order to try and displace the coordinated alkyne ligand. No observable reaction occurred even when the mixtures were refluxed in $CHCl_3$ for several hours. This suggests [19] that as expected these four-electron alkyne ligands are very strongly bonded to the metal compared with two-electron alkyne ligand complexes, in which the alkyne ligand can often be displaced.

Experimental

All reactions described in this paper were carried out under nitrogen using standard Schlenk line techniques. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) were prepared by the literature method [16]. All chemicals used in this work were obtained from commercial sources. CH_2Cl_2 was dried and distilled before use.

Elemental analyses (C, H and N) were determined with a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded either on a JEOL FX60 or a Bruker AC 250 CP/MAS NMR spectrometer, with tetramethylsilane as reference.

Preparation of $[WI_2(CO)(CN^tBu)(\eta^2\text{-}MeC_2Me)_2]$ *(1)*

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.5104 g, 0.83 mmol) in CH_2Cl_2 (15 cm^3) under nitrogen was added CN^tBu (0.069 g, 0.83 mmol). After

20 min the yellow/green solution was filtered and the solvent removed *in vacuo*. Recrystallisation from CH_2Cl_2 afforded $[WI_2(CO)(CN^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**1**). (Yield of pure product = 0.28 g, 51%.)

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with the appropriate quantities (two, three, four and five equivalents) of CN^tBu in CH_2Cl_2 at room temperature gave the complexes **3**, **5**, **7** and **9**, respectively. Reaction times were as follows: **3**: $t = 30$, **5**: $t = 40$, **7**: $t = 60$, **9**: $t = 60$ min, respectively. For yields, physical and analytical data please see Table 1.

Preparation of $[WI_2(CO)(CN^tBu)(\eta^2\text{-}PhC_2Ph)_2]$ *(2)*

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (0.50 g, 0.58 mmol) in CH_2Cl_2 (30 cm^3) under nitrogen was added CN^tBu {0.048 g, (0.035 cm^3), 0.58 mmol}. After 1 min, the solvent was removed *in vacuo* to give the green crystalline complex $[WI_2(CO)(CN^tBu)(\eta^2\text{-}PhC_2Ph)_2]$ (**2**). Complex **2** was washed with 40/60 petroleum ether and dried *in vacuo*. Recrystallisation from CH_2Cl_2 gave $[WI_2(CO)(CN^tBu)(\eta^2\text{-}PhC_2Ph)_2]$ (**2**). (Yield of pure product = 0.41 g, 78%.)

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with the appropriate quantities (two, three, four and five equivalents) of CN^tBu in CH_2Cl_2 at room temperature gave the complexes **4**, **6**, **8** and **10**, respectively. Reaction times were as follows: **4**: $t = 5$, **6**: $t = 10$, **8**: $t = 15$, **10**: $t = 20$ min, respectively. For yields, physical and analytical data see Table 1.

Acknowledgements

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