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Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with Pyridines and Related Ligands. X-ray Crystal Structure of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$

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The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) react with 1 equiv of L (L = py, 3-Cl-py, or 3,5-Me_2py) in CH_2Cl_2 at room temperature to give the substituted products $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$. Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 2 equiv of pyridine was followed by infrared spectroscopy. The initially formed mono(alkyne) complex $[WI_2(CO)(py)_2(\eta^2\text{-}MeC_2Me)]$ reacted with the displaced but-2-yne ligand to afford the cationic bis(but-2-yne) complex $[WI(CO)(py)_2(\eta^2\text{-}MeC_2Me)_2]I$. These cationic bis(alkyne) complexes containing monodentate pyridine ligands could not be isolated in a pure state. However, reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equiv of LL (LL = 2,2′-bipyridyl or 1,10-phenanthroline) in CH_2Cl_2 at room temperature gave good yields of the cationic complexes $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2]I$. The cationic complexes $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][BPh_4]$ (R = Me, Ph; LL = 2,2′-bipyridyl, 1,10-phenanthroline, *o*-phenylenediamine) were also synthesized by reacting $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with LL in the presence of $Na[BPh_4]$ in a 1:1:1 molar ratio in CH_2Cl_2 in order to confirm the ionic nature of these compounds. The structure of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ has been determined and refined to $R = 0.064$ ($R_w = 0.067$) by using 4828 independent reflections above background [crystals were triclinic, space group $P\bar{1}$; $a = 13.904$ (8), $b = 10.808$ (11), $c = 13.596$ (12) Å; $\alpha = 94.1$ (1), $\beta = 96.0$ (1), $\gamma = 94.4$ (1)°; $Z = 2$]. The molecule adopts a distorted octahedral geometry with both but-2-yne ligands cis and parallel to each other. The carbon monoxide ligand is trans to the iodide ligand with the remaining two sites being occupied by the bipyridyl nitrogen atoms, which are trans to the but-2-yne ligands. The ^{13}C NMR spectra of the $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$ and $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2]I$ type complexes indicate that the two alkyne ligands are donating a total of six electrons to the tungsten atom. The complex $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ can also react with 2 equiv of bpy followed by 2 equiv of $Na[BPh_4]$ in CH_2Cl_2 at room temperature to give the novel dicationic complex $[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2$. The diphenylacetylene ligand is donating four electrons to the metal in this compound.

Introduction

In recent years there has been considerable interest in complexes of molybdenum and tungsten containing alkynes as attached ligands.(1) It has been shown that the coordinated alkyne ligand in these complexes can function as a "four-electron" donor by utilizing both sets of filled π orbitals.(2) Although there are a large number of mono(alkyne) complexes known, far fewer bis(alkyne) complexes have been reported. This may be due to the fact that alkynes have often been used to prepare cyclobutadiene transition-metal complexes.(3) These must be formed by initial coordination of two alkyne ligands followed by an intramolecular oxidative addition to give a metallocyclopentadiene,(4) which can finally reductively form a C–C bond to give the observed cyclobutadiene complex.

We have been investigating the chemistry of the highly versatile bis(alkyne) compounds $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph),(5) and in this paper we wish to describe their reactions with pyridine and related ligands to give neutral and cationic alkyne complexes. We also report the X-ray crystal structure of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$.

Experimental Section

All syntheses were carried out on a Schlenk line. Isolated products were stored in Schlenk tubes. Methylene chloride was dried over refluxing P_2O_5 and purged with N_2 before use. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) were prepared by the literature method,(5) and all chemicals were purchased from commercial sources.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX60 or a Bruker WH-400-MHz NMR spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen, and nitrogen were recorded on a Carlo Erba MOD 1106 elemental analyzer (with helium as the carrier gas).

Syntheses. $[WI_2(CO)(py)(\eta^2\text{-}MeC_2Me)_2]$ (1). To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.500 g, 0.813 mmol), dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen, was added pyridine (0.0643 g, 0.813 mmol). After the solution was stirred for 120 min, removal of the solvent in vacuo gave brown-orange crystals of $[WI_2(CO)(py)(\eta^2\text{-}MeC_2Me)_2]$, which were recrystallized from CH_2Cl_2. Yield of pure product = 0.41 g, 61%.

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with L (L = py, 3-Cl-py, 3,5-Me_2py) gave the new complexes $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$ (**2**–**6**) (see Table III for color and yields).

$[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]I$ (7). To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.300 g, 0.488 mmol), dissolved in CH_2Cl_2 (15 cm^3) at 0 °C with continuous stirring under a stream of dry nitrogen, was added 2,2′-bipyridyl (bpy) (0.0762 g, 0.488 mmol). After the solution was stirred for 2 h, filtration and removal of the solvent in vacuo gave green crystals of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]I$ (**7**), which were recrystallized from CH_2Cl_2. Yield of pure product = 0.24 g, 66%.

A similar reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1,10-phenanthroline (1,10-phen) in CH_2Cl_2 gave the new compound $[WI(CO)(1,10\text{-}phen)(\eta^2\text{-}MeC_2Me)_2]I$ (**10**) (see Table III for color and yield).

$[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (8). To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (1.00 g, 1.626 mmol), dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen, was added bpy (0.254 g, 1.626 mmol) followed by $Na[BPh_4]$ (0.5565 g, 1.626 mmol), and the mixture was stirred for 2 h. Filtration to remove NaI and removal of the solvent in vacuo gave yellow crystals of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**8**), which were recrystallized from CH_2Cl_2. Yield of pure product = 1.41 g, 94%. Crystals of **8** were obtained for X-ray crystallography from a cooled solution of the complex (−30 °C) in acetonitrile.

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with 1 equiv of LL (LL = bpy, 1,10-phen, *o*-phen) followed by $Na[BPh_4]$ in CH_2Cl_2 gave the new complexes $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][BPh_4]$ (**9**, **11**–**14**) (see Table III for colors and yields).

$[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$ (15). To $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (0.300 g, 0.348 mmol), dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen was added bpy (0.109 g, 0.695 mmol) followed by $Na[BPh_4]$ (0.238 g, 0.695 mmol), and the mixture was stirred for 2 h. Filtration to remove NaI and removal of the solvent in vacuo gave green crystals of $[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$ (**15**), which were recrystallized from CH_2Cl_2. Yield of pure product = 0.30 g, 61%.

Crystal Data. Crystals were prepared as described above. Crystals data for **8**, $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$, $WIC_{41}H_{38}OBN_2$: M_r

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Table I. Atomic Coordinates ($\times 10^4$) for **8** with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
W(1)	2755 (0)	−2206 (1)	2168 (0)
I(2)	2883 (1)	416 (1)	2658 (1)
C(11)	2782 (10)	−4018 (19)	2338 (12)
O(12)	2757 (10)	−5079 (12)	2424 (11)
C(13)	3875 (17)	−694 (22)	463 (17)
C(14)	3537 (11)	−1740 (16)	1012 (12)
C(15)	3534 (9)	−2950 (16)	1055 (10)
C(16)	3844 (14)	−4124 (17)	589 (14)
C(17)	853 (13)	−4298 (18)	1115 (15)
C(18)	1406 (9)	−3061 (15)	1464 (11)
C(19)	1388 (10)	−1894 (16)	1489 (13)
C(20)	739 (13)	−928 (19)	1161 (16)
N(21)	4107 (10)	−1946 (12)	3290 (10)
C(22)	5027 (10)	−1694 (17)	3034 (14)
C(23)	5817 (12)	−1437 (20)	3659 (18)
C(24)	5721 (15)	−1473 (20)	4674 (19)
C(25)	4803 (17)	−1713 (20)	4923 (15)
C(26)	4005 (12)	−1948 (17)	4261 (14)
C(27)	3012 (12)	−2138 (15)	4481 (12)
N(28)	2279 (9)	−2217 (12)	3690 (9)
C(29)	1364 (11)	−2355 (18)	3893 (15)
C(30)	1095 (18)	−2463 (20)	4807 (16)
C(31)	1844 (19)	−2435 (19)	5592 (14)
C(32)	2800 (16)	−2273 (21)	5468 (17)
B(1)	7712 (13)	5638 (17)	2516 (15)
C(61)	8632 (9)	4743 (14)	2482 (11)
C(62)	8668 (10)	3840 (15)	1705 (13)
C(63)	9401 (16)	3046 (20)	1642 (17)
C(64)	10125 (17)	3085 (20)	2441 (18)
C(65)	10155 (11)	3967 (19)	3236 (15)
C(66)	9409 (13)	4764 (17)	3246 (13)
C(71)	8042 (10)	6793 (16)	3430 (12)
C(72)	8398 (11)	7983 (18)	3236 (17)
C(73)	8719 (19)	8965 (22)	3940 (20)
C(74)	8603 (19)	8768 (27)	4867 (23)
C(75)	8227 (16)	7662 (30)	5138 (14)
C(76)	7990 (12)	6692 (20)	4401 (13)
C(81)	6724 (10)	4844 (16)	2737 (13)
C(82)	6023 (13)	5306 (20)	3305 (17)
C(83)	5146 (15)	4693 (22)	3398 (21)
C(84)	4854 (15)	3565 (25)	2903 (20)
C(85)	5486 (14)	3069 (22)	2307 (17)
C(86)	6404 (13)	3678 (17)	2221 (13)
C(91)	7516 (11)	6302 (13)	1487 (12)
C(92)	8205 (14)	6496 (16)	848 (14)
C(93)	8012 (16)	7114 (17)	−18 (15)
C(94)	7135 (16)	7484 (16)	−270 (13)
C(95)	6391 (14)	7306 (17)	325 (14)
C(96)	6608 (11)	6685 (15)	1203 (12)

= 896.3; triclinic; $a = 13.904$ (8), $b = 10.808$ (11), $c = 13.596$ (12) Å; $\alpha = 94.1$ (1), $\beta = 96.0$ (1), $\gamma = 94.4$ (1)°; $V = 2019.2$ Å^3, $d_c = 1.49$ g cm^{-3}, $d_m = 1.54$ g cm^{-3}, $F(000) = 876$, $Z = 2$, $\lambda = 0.7107$ Å, $\mu = 38.62$ cm^{-1}, space group $P\bar{1}$.

A crystal of approximate size 0.25 × 0.3 × 0.3 mm was set up to rotate about the axis on a Stoe Stadi2 diffractometer, and data were collected via variable-width ω scan. Background counts were for 20 s, and a scan rate of 0.0333°/s was applied to a width of (1.5 + (sin μ/tan θ))°. A total of 6298 independent reflections were measured, of which 4828 with $I > 3\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied.[6] The structure was determined by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions although the methyl hydrogen atoms were refined as rigid groups.

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.064 ($R_w = 0.067$). Calculations were carried out by using SHELX 76[7] and some of our own programs on the Amdahl V7 at the University of Reading. Positional parameters are given in Table I, and molecular dimensions in the coordination sphere, in Table II.

Table II. Molecular Dimensions in the Coordination Sphere of **8**: Distances, Å; Angles, deg

W(1)–I(2)	2.852 (1)	W(1)–C(18)	2.126 (12)
W(1)–C(11)	1.991 (20)	W(1)–C(19)	2.087 (15)
W(1)–C(14)	2.073 (17)	W(1)–N(21)	2.279 (13)
W(1)–C(15)	2.101 (14)	W(1)–N(28)	2.238 (13)
I(2)–W(1)–C(11)	159.9 (5)	C(18)–W(1)–C(19)	34.9 (6)
I(2)–W(1)–C(14)	84.4 (5)	I(2)–W(1)–N(21)	78.9 (3)
C(11)–W(1)–C(14)	109.8 (6)	C(11)–W(1)–N(21)	86.1 (5)
I(2)–W(1)–C(15)	120.3 (4)	C(14)–W(1)–N(21)	92.4 (5)
C(11)–W(1)–C(15)	73.2 (6)	C(15)–W(1)–N(21)	92.0 (5)
C(14)–W(1)–C(15)	36.7 (6)	C(18)–W(1)–N(21)	157.1 (5)
I(2)–W(1)–C(18)	117.3 (4)	C(19)–W(1)–N(21)	158.5 (5)
C(11)–W(1)–C(18)	74.0 (5)	I(2)–W(1)–N(28)	81.3 (3)
C(14)–W(1)–C(18)	104.7 (5)	C(11)–W(1)–N(28)	81.3 (5)
C(15)–W(1)–C(18)	92.8 (5)	C(14)–W(1)–N(28)	160.5 (5)
I(2)–W(1)–C(19)	82.9 (5)	C(15)–W(1)–N(28)	150.8 (5)
C(11)–W(1)–C(19)	108.5 (6)	C(18)–W(1)–N(28)	93.6 (5)
C(14)–W(1)–C(19)	97.1 (6)	C(19)–W(1)–N(28)	94.2 (5)
C(15)–W(1)–C(19)	107.1 (5)	N(21)–W(1)–N(28)	71.9 (5)

Results

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) react in CH_2Cl_2 at room temperature with 1 equiv of L (L = py, 3-Cl-py, 3,5-Me_2py) to afford good yields of the new substituted compounds $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$ (**1–6**). However, reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with 1 equiv of the bidentate nitrogen donor ligands LL [LL = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (1,10-phen), *o*-phenylenediamine (*o*-phen)] in CH_2Cl_2 at room temperature in the presence of $Na[BPh_4]$ gives the new cationic bis(alkyne) compounds $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][BPh_4]$ (**8**, **9**, **11–14**). The complexes with iodide as the counteranion have been isolated for R = Me and LL = bpy and 1,10-phen. The compound $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ when reacted with 2 equiv of bpy followed by 2 equiv of $Na[BPh_4]$ in CH_2Cl_2 at room temperature gives the new dicationic complex $[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$ (**15**). All the new complexes (**1–15**) have been fully characterized by elemental analysis (C, H, and N) (Table III), IR spectroscopy (Table IV), and ^{1}H and ^{13}C NMR spectroscopy (Tables V and VI). Complexes **1**, **3**, **5**, **9**, **11**, **12**, and **15** were confirmed as $^1/_2$ CH_2Cl_2, CH_2Cl_2, or 2 CH_2Cl_2 solvates by repeated elemental analyses and ^{1}H NMR spectroscopy. The structure of the complex $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**8**) has been determined by X-ray crystallography.

Discussion

Reaction of the Complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with Pyridines. The new mono(pyridine) complexes $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$ (L = py, 3-Cl-py, 3,5-Me_2py; R = Me, Ph) are all formed from the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ and L. The structure of complexes **1–6** is likely to be similar to that of the compounds $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph), which have been determined by X-ray crystallography.[5] They have two cis iodide ligands trans to the perpendicular cis alkyne ligands, with acetonitrile and carbon monoxide occupying the other two octahedral sites. These reactions could proceed by either an associative or a dissociative mechanism, but it has been shown that acetonitrile is not lost from $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ by a dissociative mechanism to afford $[W(\mu\text{-}I)I(CO)(\eta^2\text{-}RC_2R)_2]_2$, even after refluxing in $CHCl_3$ for 24 h.[5] However, the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with pyridine is rapid, and an associative seven-coordinate adduct, $[WI_2(CO)(NCMe)L(\eta^2\text{-}RC_2R)_2]$, can be postulated, with each alkyne ligand donating two electrons to the metal. Loss of acetonitrile from the intermediate would allow the bonding of the alkyne ligands to revert to "three-electron" donors.

Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with 2-equiv samples of pyridine is more interesting. For example, the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 2 equiv of pyridine in CH_2Cl_2 at room temperature has been followed by infrared spectroscopy. The infrared spectrum after 2 min shows a strong carbonyl band at 2055 cm^{-1} due to $[WI_2(CO)(py)(\eta^2\text{-}MeC_2Me)_2]$

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Table III. Physical and Analytical Data[a] for $[WI_2(CO)L(\eta^2\text{-}RC_2R)_2]$, $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][X]$, and $[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$

no.	complex	color	yield, %	% C	% H	% N
1	$[WI_2(CO)(py)(\eta^2\text{-}MeC_2Me)_2]\cdot 2CH_2Cl_2$	brown-orange	61	23.3 (23.4)	2.7 (2.6)	1.8 (1.7)
2	$[WI_2(CO)(py)(\eta^2\text{-}PhC_2Ph)_2]$	brown-green	63	45.6 (45.3)	3.3 (2.8)	1.9 (1.6)
3	$[WI_2(CO)(3\text{-}Cl\text{-}py)(\eta^2\text{-}MeC_2Me)_2]\cdot 2CH_2Cl_2$	yellow	85	22.4 (22.4)	2.3 (2.4)	2.0 (1.6)
4	$[WI_2(CO)(3\text{-}Cl\text{-}py)(\eta^2\text{-}PhC_2Ph)_2]$	dark green	61	43.5 (43.6)	2.8 (2.6)	1.9 (1.5)
5	$[WI_2(CO)(3,5\text{-}Me_2py)(\eta^2\text{-}MeC_2Me)_2]\cdot CH_2Cl_2$	green	59	26.6 (26.7)	3.2 (3.0)	2.1 (1.8)
6	$[WI_2(CO)(3,5\text{-}Me_2py)(\eta^2\text{-}PhC_2Ph)_2]$	dark green	80	46.2 (46.5)	3.4 (3.1)	1.7 (1.5)
7	$[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]I$	green	66	31.3 (31.3)	2.9 (2.8)	3.4 (3.8)
8	$[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$	yellow	94	55.9 (56.0)	4.5 (4.4)	3.0 (3.0)
9	$[WI(CO)(bpy)(\eta^2\text{-}PhC_2Ph)_2][BPh_4]\cdot {}^1/_2CH_2Cl_2$	green	64	61.9 (62.9)	4.1 (4.2)	2.3 (2.3)
10	$[WI(CO)(1,10\text{-}phen)(\eta^2\text{-}MeC_2Me)_2]I$	orange	62	33.6 (33.4)	3.1 (2.7)	3.7 (3.7)
11	$[WI(CO)(1,10\text{-}phen)(\eta^2\text{-}MeC_2Me)_2][BPh_4]\cdot {}^1/_2CH_2Cl_2$	brown	66	55.2 (55.3)	4.4 (4.2)	2.6 (2.8)
12	$[WI(CO)(1,10\text{-}phen)(\eta^2\text{-}PhC_2Ph)_2][BPh_4]\cdot CH_2Cl_2$	brown	70	62.1 (62.0)	4.1 (3.9)	2.1 (2.2)
13	$[WI(CO)(o\text{-}phen)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$	brown-green	50	53.2 (53.6)	4.3 (4.6)	3.4 (3.2)
14	$[WI(CO)(o\text{-}phen)(\eta^2\text{-}PhC_2Ph)_2][BPh_4]$	orange	55	63.2 (63.1)	4.3 (4.3)	2.7 (2.5)
15	$[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$	green	60	70.6 (70.8)	4.7 (4.8)	4.0 (3.9)

[a] Calculated values in parentheses.

Table IV. IR Data[a] for $[WI_2(CO)(L)(\eta^2\text{-}RC_2R)_2]$, $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][X]$, and $[W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)][BPh_4]_2\cdot CH_2Cl_2$

complex	ν(CO), cm^{-1}	ν(C≡C), cm^{-1}	complex	ν(CO), cm^{-1}	ν(C≡C), cm^{-1}
1	2055 (s)	1635 (w)	**9**	2098 (s)	1662 (vw)
2	2095 (s)	1615 (vw)	**10**	2050 (s)	1630 (vw)
3	2060 (s)	1620 (vw)	**11**	2050 (s)	1633 (vw)
4	2090 (s)	1650 (vw)	**12**	2080 (s)	1630 (vw)
5	2050 (s)	1620 (vw)	**13**	2055 (s)	1632 (vw)
6	2098 (s)	1648 (vw)	**14**	2090 (s)	1630 (vw)
7	2052 (s)	1660 (vw)	**15**	1963 (s)	1692 (w)
8	2052 (s)	1658 (vw)			

[a] All spectra recorded in $CHCl_3$. Key: s, strong; w, weak; vw, very weak.

(**1**) and a much weaker band at lower wavenumber (1915 cm^{-1}). This is almost certainly due to the alkyne-substituted product $[WI_2(CO)(py)_2(\eta^2\text{-}MeC_2Me)]$. This complex is analogous to the bis(pyridine) complex $[MoCl_2(CO)(py)_2(\eta^2\text{-}MeC_2Me)]$ (ν(CO)(CH_2Cl_2) = 1937 cm^{-1}) reported by Templeton and coworkers.[8] However, after 30 min the carbonyl band due to $[WI_2(CO)(py)_2(\eta^2\text{-}MeC_2Me)]$ reaches a maximum (still only about two-thirds of the intensity of the band due to **1**). A proton NMR spectrum of this reaction mixture shows two broad doublets at 3.00 and 2.55 ppm (intensity ratio 3:2), due to the methyl protons in **1** and $[WI_2(CO)(py)_2(\eta^2\text{-}MeC_2Me)]$, respectively. After further reaction for 1 h, the band due to **1** decreases and a new band at 2040 cm^{-1} is observed. This band at 2040 cm^{-1} is likely to be due to the cationic bis(alkyne) compound $[WI(CO)(py)_2(\eta^2\text{-}MeC_2Me)_2]I$, which can be formed by displacement of the iodide ligand by but-2-yne. Many attempts were made to isolate and characterize complexes of the types $[WI_2(CO)L_2(\eta^2\text{-}RC_2R)]$ and $[WI(CO)L_2(\eta^2\text{-}RC_2R)_2]I$ without success. These complexes are very unstable. However, reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with bidentate nitrogen donor ligands gave high yields of the new cationic complexes $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2]I$ (see next section), which were considerably more stable than their pyridine analogues.

Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with Bidentate Nitrogen Donor Ligands. The reaction of the complex $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equiv of bpy in CH_2Cl_2 at 0 °C has been followed by infrared spectroscopy. After 7 min the carbonyl band due to $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ decreases in intensity and a new carbonyl band at 1992 cm^{-1} is observed. This can be ascribed to the monodentate coordinated bpy complex $[WI_2(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]$. The carbonyl band at 1992 cm^{-1} decreases in intensity, and a new band at 1918 cm^{-1} due to the alkyne-displaced complex $[WI_2(CO)(bpy)(\eta^2\text{-}MeC_2Me)]$ is observed. After 17 min the carbonyl band due to $[WI_2(CO)(bpy)(\eta^2\text{-}MeC_2Me)]$ disappears to eventually give a spectrum with a single carbonyl band at 2052 cm^{-1} due to the cationic bis(alkyne) complex $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]I$ (**7**). The but-2-yne ligand reenters the coordination sphere via displacement of the weakly bonded iodide ligand. The proposed mechanism from the infrared evidence given above is shown in Scheme I. The complex shown with the iodide trans to a bipyridyl nitrogen atom must rearrange, probably by a trigonal twist mechanism, to give the thermodynamically more stable isomer shown in Figure 1. It is interesting to note that Templeton and co-workers[8] did not observe any evidence for a cationic bis(but-2-yne) complex from reaction of $[MoCl_2(CO)_3(py)_2]$ with excess but-2-yne. It is well-known that iodide ligands are more easily displaced than chloride or bromide ligands from neutral organotransition-metal complexes, due to a weaker M–I bond strength. As expected, the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ react with bidentate nitrogen donor ligands in the presence of $Na[BPh_4]$ (at +20 °C) to directly give the cationic bis(alkyne) complexes $[WI(CO)(LL)(\eta^2\text{-}RC_2R)_2][BPh_4]$. There was no evidence for the neutral intermediates from IR studies, and thus $Na[BPh_4]$ promotes iodide displacement to create a vacant site for the bidentate nitrogen donor ligand to fill.

The reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with 2 equiv of bpy followed by 2 equiv of $Na[BPh_4]$ in CH_2Cl_2 gave a good yield of the novel dicationic complex $[W(CO)(bpy)_2(\eta^2\text{-}$

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(8) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707.

Table V. ^{1}H NMR Data[a-c] for $[\mathrm{WI_2(CO)L(\eta^2\text{-}RC_2R)_2}]$, $[\mathrm{WI(CO)(LL)(\eta^2\text{-}RC_2R)_2}][\mathrm{X}]$, and $[\mathrm{W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)}][\mathrm{BPh_4}]_2\cdot\mathrm{CH_2Cl_2}$

compd	^{1}H δ
1	2.95, 3.02 (d, 12 H, *Me*$\mathrm{C_2}$); 5.31 (s, 4 H, C*H*$_2$Cl$_2$); 8.13, 8.04 (d, 2 H, *o-py*); 8.59 (s, 1 H, *p-py*); 9.18, 9.08 (d, 2 H, *m-py*)
2	7.4 (br m, 20 H, *Ph*C$_2$); 8.39, 8.53 (br m, 5 H, *py*)
3	2.93 (s, 6 H, *Me*C$_2$); 3.21 (s, 6 H, *Me*C$_2$); 5.3 (s, 4 H, C*H*$_2$Cl$_2$); 7.74 (m, 1 H$_5$, *py*); 8.18 (m, 1 H$_4$, *py*); 9.5 (br s, 1 H$_6$, *py*); 9.89 (br s, 1 H$_2$, *py*)
4	7.4 (br m, 20 H, *Ph*C$_2$); 8.26 (br s, H$_5$, *py*); 9.14 (br m, 1 H$_4$, *py*); 9.39 (br m, 1 H$_6$, *py*); 9.8 (br m, 1 H$_2$, *py*)
5	2.61 (s, 6 H, *Me*); 2.9 (s, 6 H, *Me*C$_2$); 3.14 (s, 6 H, *Me*C$_2$); 5.32 (s, 2 H, C*H*$_2$Cl$_2$); 8.21 (s, 1 H$_4$, *py*); 8.63 (br s, 2 H$_{2,6}$, *py*)
6	2.48 (s, 6 H, *Me*); 7.36 (br m, 20 H, *Ph*C$_2$); 8.03 (br s, 1 H$_4$, *py*); 8.45 (br s, 2 H$_{2,6}$, *py*)
7	3.27 (s, 6 H, *Me*C$_2$); 3.55 (s, 6 H, C$_2$*Me*); 7.75, 7.82 (d, 2 H$_{5,8}$, *bpy*); 8.30, 8.38 (br d, 2 H$_{3,10}$, *bpy*); 8.77, 8.86, 8.99, 9.09 (br m, 4 H$_{4,9,2,11}$, *bpy*)
8	3.01 (s, 6 H, *Me*C$_2$); 3.46 (s, 6 H, C$_2$*Me*); 6.86, 6.96 (m, 8 H, *o-Ph*); 7.53 (br m, 12 H, *Ph*, and 8 H, *bpy*)
9	5.28 (s, 1 H, C*H*$_2$Cl$_2$); 6.80, 6.82 (d, 8 H, *o-Ph*); 7.4 (br m, 24 H, *Ph*, 20 H, *Ph*C$_2$, and 2 H$_{5,8}$, *bpy*); 7.62 (d, 2 H$_{3,10}$, *bpy*); 7.77 (d, 2 H$_{4,9}$, *bpy*); 8.24, 8.26 (d, 2 H$_{2,11}$, *bpy*)
10	3.15, 3.29 (m, 12 H, *Me*C$_2$); 8.23 (br m, 4 H$_{3,6,7,10}$, *1,10-phen*); 8.83 (br m, 2 H$_{2,9}$, *1,10-phen*); 9.67 (d, 2 H$_{1,10}$, *1,10-phen*)
11	3.29 (s, 12 H, *Me*C$_2$), 5.26 (s, 1 H, C*H*$_2$Cl$_2$); 6.85 (br s, 8 H, *o-Ph*); 7.48 (br m, 12 H, *Ph*); 7.96, 7.85 (d, 4 H$_{3,6,7,10}$, *1,10-phen*); 8.27 (s, 2 H$_{4,9}$, *1,10-phen*); 10.17 (br s, 2 H$_{1,10}$, *1,10-phen*)
12	5.29 (s, 2 H, C*H*$_2$Cl$_2$); 6.76, 6.87 (m, 8 H, *o-Ph*); 7.47 (br m, 12 H, *Ph*); 7.81, 7.82 (d, 4 H$_{3,6,7,10}$, *1,10-phen*); 8.15 (d, 2 H$_{4,9}$, *1,10-phen*); 8.27 (d, 2 H$_{4,9}$, *1,10-phen*); 8.45 (d, 2 H$_{1,10}$, *1,10-phen*)
13	2.88 (br s, 12 H, *Me*C$_2$); 6.9, 7.03 (br d, 8 H, *o-Ph*); 7.48 (br s, 12 H, *Ph*, and 4 H, *o-phen*)
14	6.45 (br s, 2 H, N*H*); 6.86 (br m, 8 H, *o-Ph*); 7.51 (br m, 12 H, *Ph*, 10 H, *Ph*C$_2$, and 2 H, *o-phen*); 7.79, 7.81 (d, 2 H, *o-phen*)
15	5.29 (s, 2 H, C*H*$_2$Cl$_2$); 6.82, 6.91 (br d, 16 H, *Ph*); 7.35, 7.4 (br m, 54 H, *Ph*C$_2$, and *Ph*); 8.00 (s, 4 H$_{5,8}$, *bpy*); 8.47 (d, 2 H$_{4,9}$, *bpy*); 8.56 (d, 2 H$_{2,11}$, *bpy*)

[a] Spectra recorded in $\mathrm{CDCl_3}$ (+25 °C) referenced to $\mathrm{Me_4Si}$. [b] Analyses of ^{1}H NMR spectra as shown in Figure 2 were made from information taken from: Bovey, F. A. *NMR Data Tables for Organic Compounds*; Wiley: New York, 1967; Vol. 1. [c] *o*-py = py H$_{2,6}$; *p*-py = py H$_4$; *m*-py = py H$_{3,5}$; *o*-Ph = Ph ortho H.

Table VI. Selected ^{13}C NMR Data[a,b] for $[\mathrm{WI_2(CO)(L)(\eta^2\text{-}RC_2R)_2}]$, $[\mathrm{WI(CO)(LL)(\eta^2\text{-}RC_2R)_2}][\mathrm{X}]$, and $[\mathrm{W(CO)(bpy)_2(\eta^2\text{-}PhC_2Ph)}][\mathrm{BPh_4}]_2\cdot\mathrm{CH_2Cl_2}$

compd	^{13}C δ
2	200.21 (s, *C*O); 174.78, 163.86 (s, $C\equiv C$); 147.0 (s, *o-py*); 141.0 (s, *p-py*); 139.69 (*m-py*); 137.1, 135.41 (s, *Ph*C$_2$); 128.78, 128.52, 128.0, 127.74 (m, *Ph*)
4	200.38 (s, *C*O); 180.63, 174.78, 169.84, 163.73 (s, $C\equiv C$); 159.06 (s, Cl-*py*); 158.15 (s, *o*-Cl-py); 146.32 (s, *o*-Cl, N*C*, *py*); 140.47 (s, *m-py*); 136.97 (s, *o-py*); 129.82, 128.65, 127.61, 127.09 (m, *Ph*)
6	200.83 (s, *C*O); 179.6, 174.65, 167.63, 163.6 (s, $C\equiv C$); 148.01, 145.28 (s, Me*py*); 139.3, 137.61 (s, *o-py*); 136.84 (s, *p-py*); 131.0 (s, *Ph*); 129.43, 128.52, 127.48 (m, *Ph*); 18.84 (s, *Me*)
8	220.01 (s, *C*O); 175.29, 153.08 (s, $C\equiv C$); 142.42, 141.25, 138.52, 135.93, 134.76 (m, *bpy*); 131.12, 128.78, 128.39, 128.0, 127.35, 125.92 (m, *Ph*); 122.02 (s, *Ph*); 53.53 (s, *C*H$_2$Cl$_2$); 24.82, 18.58 (s, *Me*C$_2$)
9[c]	199.56 (s, *C*O); 189.75, 150.20 (s, $C\equiv C$); 142.0, 139.49, 138.33, 135.60, 135.40 (m, *bpy*); 131.39, 129.16, 128.81, 128.53, 128.12, 127.36 (m, *Ph*); 57.09 (s, *C*H$_2$Cl$_2$)
11	210.38 (s, *C*O); 184.79, 149.7 (s, $C\equiv C$); 140.86, 138.39, 136.19, 135.8, 134.63 (m, *1,10-phen*); 130.99 (s, *Ph*); 128.26, 127.87, 127.22, 125.79 (m, *Ph*); 57.09 (s, *C*H$_2$Cl$_2$); 29.63, 26.25 (s, *Me*C$_2$)
13	208.88 (s, *C*O); 175.04 (s, $C\equiv C$); 138.14, 136.19, 135.8, 134.63 (m, *o-phen*); 130.6, 128.26, 127.87, 127.39, 125.79 (m, *P*h); 17.28, 15.2 (s, *M*eC$_2$)
15	227.01 (s, $C\equiv C$); 209.00 (s, *C*O); 129.04 (br m, *Ph* and bpy) ; 57.09 (*C*H$_2$Cl$_2$)

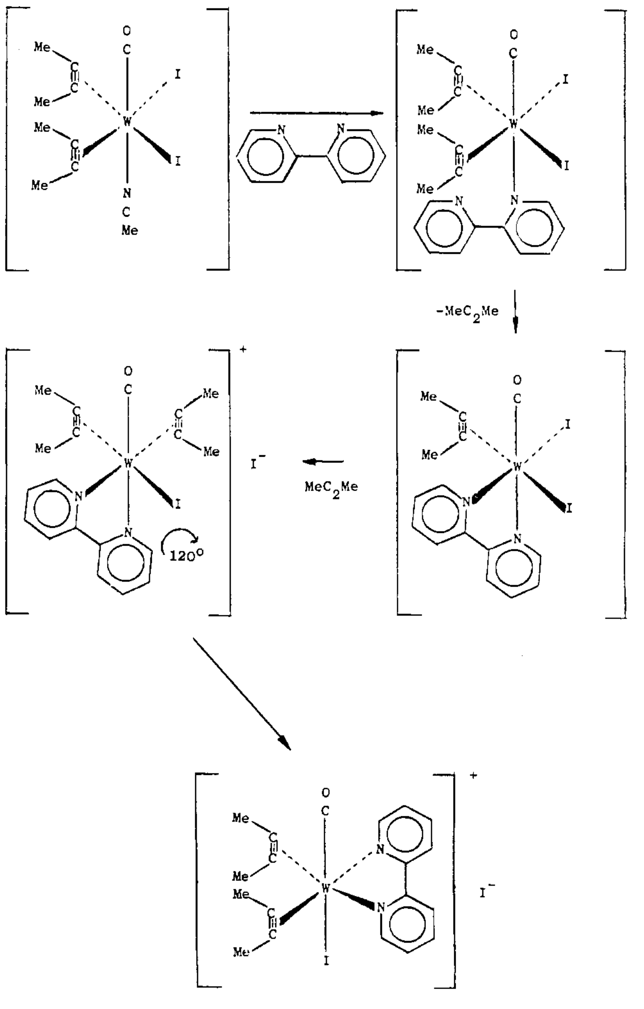
[a] Spectra recorded in $\mathrm{CDCl_3}$ (+25 °C) referenced to $\mathrm{Me_4Si}$. [b] *o*-py = py C$_{2,6}$; *p*-py = py C$_4$; *m*-py = py C$_{3,5}$. [c] Spectrum run on the Bruker WH-400 at the University of Warwick.

$\mathrm{MeC_2Me)}][\mathrm{BPh_4}]_2$. The likely structure of this complex has the carbonyl and alkyne ligands cis to each other.

Several attempts were made to reduce the cationic bis(alkyne) complex $[\mathrm{WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2}][\mathrm{BPh_4}]$ (**8**) by using Na/Hg and $\mathrm{Na}[\mathrm{Fe(CO)_2(\eta^5\text{-}C_5H_5)}]$, which have previously been used as one-electron reducing agents;[9] however, no tungsten organometallic complexes were isolated from these reactions.

Description of the Molecular Structure of $[\mathbf{WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2}][\mathbf{BPh_4}]$ (8). The structure is shown in Figure 1 together with the atomic numbering scheme. The tungsten atom is bonded to an iodine and a trans carbonyl group [W–C(11) = 1.991 (20), W–I(2) = 2.852 (1) Å], a bipyridyl ligand [W–N(21) = 2.279 (13), W–N(28) = 2.238 (13) Å], and two dimethylalkynes [W–C(14) = 2.073 (17), W–C(15) = 2.101 (14) Å; W–C(18) = 2.126 (12), W–C(19) = 2.087 (15) Å]. The coordination geometry around the tungsten atom is probably best considered as octahedral with each alkyne occupying one coordination site trans to a nitrogen atom of the bipyridyl ligand. Thus, angles subtended at the tungsten atom from the midpoints of the alkynes [CM(1) = midpoint of C(14)–C(15); CM(2) = midpoint of C(18)–C(19)] to the appropriate nitrogen atoms are CM(1)–W–N(28) = 162.9

Scheme I



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(9) Brammer, L.; Green, M.; Orpen, A. G.; Paddick, K. E.; Saunders, D. R. *J. Chem. Soc., Dalton Trans.* **1986**, 657.

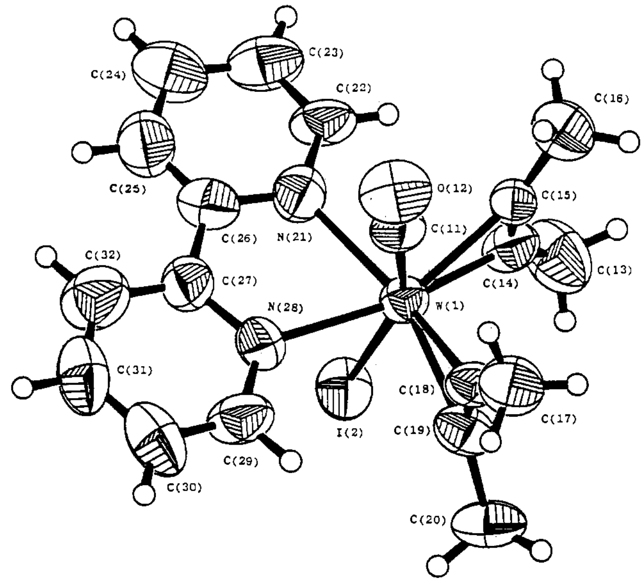

Figure 1. Structure of $[WI(CO)(bpy)(\eta^2\text{-}MeC_2Me)_2]^+$ (Ellipsoids shown at 50% probability).

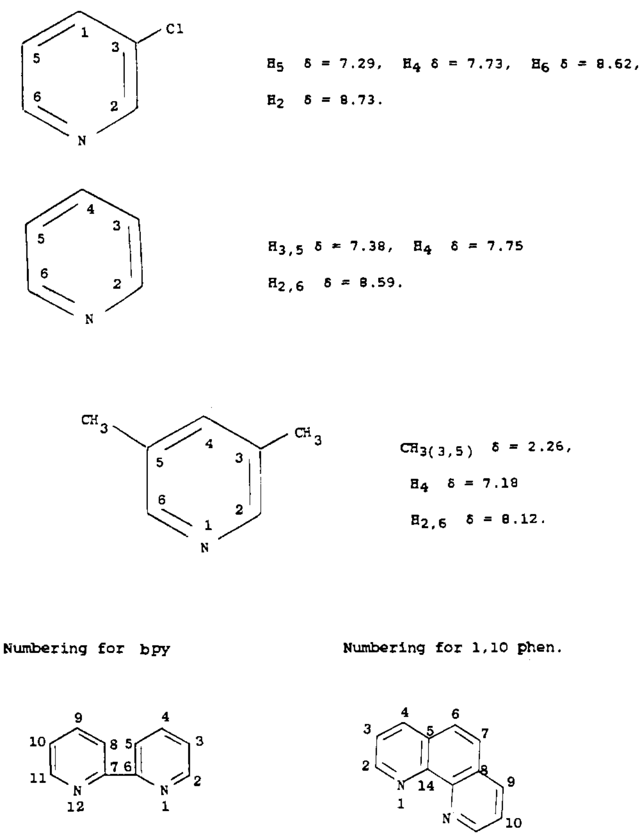

Figure 2. Atom-numbering scheme for the nitrogen-containing ligands.

(5) and CM(2)–W–N(21) = 166.0 (7)°. The two alkyne moieties are each planar and intersect the W(bpy) plane at angles of 89.9 and 85.3°, respectively. It is interesting that CM(1) is 0.41 Å but CM(2) is only 0.05 Å from this plane. It should be noted however that the bipyridyl ligand is not planar, and indeed, the two six-membered rings (planar within experimental error) intersect at an angle of 7.8°. We note however that CM(2) is 0.35 Å from the ligand adjacent six-membered ring and CM(1) is 0.21 Å from the other ring. This indicates as a possible reason for the distortion the steric effects of the bidentate ligand. CM(1) and CM(2) are distorted from the equatorial plane toward the carbonyl group and away from the iodine atom.

It is interesting that both alkyne groups are asymmetrically bonded with one W–C bond longer than the other [viz. W–C(15) = 2.101 (14), W–C(18) = 2.126 (17) Å and W–C(14) = 2.073 (17), W–C(19) = 2.087(15) Å]. In the two structures[5] of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) where the alkynes are trans to iodine, this bonding asymmetry is also found. In those two structures the two shorter bonds were both closer to the acetonitrile than to the carbonyl. In the present molecule, the two shorter bonds are closer to the iodine than to the carbonyl group [C(14)–W–I(2) = 84.4 (5), C(19)–W–I(2) = 82.9 (5)° vs C(15)–W–I(2) = 120.3 (4), C(18)–W–I(2) = 117.3 (4)°]. This common effect seems more likely to be electronic than steric and could be due to the strength of the cis carbonyl bond.

Remaining dimensions in the structure are as expected. The two alkynes retain multiple-bond character with central bond lengths of 1.31 (2) and 1.26 (2) Å. The C–C–C angles are 143.6 (14), 143.5 (17), 145.2 (14), and 140.4 (14)°.

The conformation of the tetraphenylborate ions is as expected. There are no intermolecular distances less than the sum of van der Waals radii between the ions.

Infrared Spectra. The IR spectra of complexes **1–6** all show a single carbonyl band above 2000 cm^{-1} (Table IV). These bands are at slightly higher wavenumber compared to the mono(acetonitrile) compounds $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$. This was expected, since pyridine is a stronger π-acceptor ligand than acetonitrile. The IR spectra also show a weak band at ≃1650 cm^{-1} for the C≡C stretch. This is at considerably lower wavenumber than those for the uncoordinated alkyne ligands. It is well-known that alkyne ligands can act as π-acceptor ligands, which results in a change in hybridization of the coordinated alkyne ligands. The X-ray crystal structure of **8** shown in Figure 1 also shows this change in hybridization, which results in the methyl groups bending away from the plane of the but-2-yne ligand in contrast to the structure of uncoordinated but-2-yne, which is linear.

NMR Spectra. The room-temperature ^1H NMR spectra (Table V) of **1–15** all showed the expected features for the static structures of **1–15**. The ^{13}C NMR spectrum of **11**, for example, showed two alkyne contact carbon resonances at δ = 184.79 and 149.70, which suggests that each alkyne is donating three electrons to the metal.[10] This also agrees with complexes **1–6** obeying the effective atomic number rule. Similarly, the cationic bis(alkyne) complexes **7–14** also have ^{13}C NMR chemical shifts for the contact alkyne carbon atoms in the region expected for "three-electron" alkyne ligands.

In order for the dicationic complex **15** to obey the effective atomic number rule, the alkyne ligand must donate four electrons, which is suggested by the very low alkyne contact carbon shift at 227.01 ppm.

Acknowledgments. We wish to thank Dr. O. W. Howarth for running a ^{13}C NMR spectrum at the University of Warwick, and we thank the SERC for support.

Registry No. **1**, 113949-11-4; **2**, 113949-12-5; **3**, 113949-13-6; **4**, 113975-15-8; **5**, 113949-14-7; **6**, 113949-15-8; **7**, 113949-16-9; **8**, 114029-39-9; **9**, 113949-18-1; **10**, 113975-16-9; **11**, 114030-31-8; **12**, 113975-18-1; **13**, 113949-20-5; **14**, 113949-22-7; **15**, 113949-24-9; $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$, 111187-48-5; $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$, 111187-50-9.

Supplementary Material Available: Listings of the remaining dimensions of the cation not included in the paper, dimensions of the anion, anisotropic and isotropic thermal parameters, and hydrogen coordinates (9 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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(10) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.