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Bis(alkyne) complexes of the type $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ ($R = Et$, ${}^tBu$, Ph or CH_2Ph; $R' = Me$ or Ph). X-ray crystal structure of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$

Paul K. Baker [a,*], Mary E. Harman [b], Michael B. Hursthouse [b], Aidan J. Lavery [c], K.M. Abdul Malik [b], David J. Muldoon [a], Andrew Shawcross [c]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff, CF1 3TB, UK*
[c] *ZENECA Specialities, PO Box 42, Hexagon House, Blackley, Manchester M9 3DA, UK*

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Abstract

Reaction of $[WI_2(CO)_3(NCR)_2]$ ($R = Et$, ${}^tBu$, Ph or CH_2Ph) with an excess of but-2-yne or two equivalents of PhC_2Ph in CH_2Cl_2 at room temperature gave the bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ ($R' = Me$ or Ph) (**1–8**). The crystal structure of the ^{t}butylnitrile complex $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**3**) was determined by X-ray crystallography. The geometry about the tungsten can be considered to be octahedral, with the but-2-yne ligands, as expected, *cis-* and parallel to each other and *trans-* to the two iodo-ligands, leaving the acetonitrile and carbonyl ligands mutually *trans-*. The alkyne ligands in these complexes donate a total of six-electrons to the metal, as suggested by ^{13}C NMR spectroscopy.

Keywords: Tungsten; Carbonyl; Nitrile; Alkyne; X-ray crystal structure; Diiodo

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1. Introduction

Generally, when more than one alkyne ligand is coordinated to a transition-metal centre, π-cyclobutadiene complexes are eventually formed [1]. However, when molybdenum or tungsten organotransition-metal complexes are treated with an excess of alkynes bis- or tris (alkyne) complexes are usually obtained. For example, as early as 1963, Tate and Augl [2] described the reaction of the tris(acetonitrile) complex *fac*-$[W(CO)_3(NCMe)_3]$ with an excess of EtC_2Et in refluxing hexane to give the zero-valent tris (hex-3-yne) complex $[W(CO)(\eta^2\text{-}EtC_2Et)_3]$. In 1977, Green and Bottrill [3] described the reactions of $[\{Mo(CO)_3(Cp \text{ or } C_9H_7)\}_2]$ with two equivalents of $Ag[BF_4]$ in the presence of excess RC_2R' ($R = R' = Me$ or Ph; $R = H$, $R' = Me$; $R = H$, $R' = {}^tBu$) to give the cationic bis(alkyne) complexes $[Mo(CO)(\eta^2\text{-}RC_2R')_2\{Cp \text{ or } C_9H_7\}][BF_4]$. In 1985, Davidson and Vasapollo [4] reported the reactions of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ with RC_2R' ($R = R' = Me$, Et or Ph) or PhC_2Me to give the dimeric bis(alkyne) complexes $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2\}_2]$. More recently, in 1988 [5] we described the reactions of $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) with an excess of RC_2R' ($R = R' = Ph$ or Me; $R = Me$, $R' = Ph$; for $M = W$, $R = R' = Me$, CH_2Cl or p-Tol; $R = Ph$, $R' = CH_2OH$) to give either $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ or $[\{Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2\}_2]$.

In this paper we expand on the work we reported in 1988 [5], and describe the preparation and characterisation of the bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ ($R = Et$, ${}^tBu$, Ph or CH_2Ph; $R' = Me$ or Ph) which was crystallographically characterised for $R = {}^tBu$, $R' = Me$.

2. Results and discussion

The starting materials for this research, namely $[WI_2(CO)_3(NCR)_2]$ ($R = Et$, ${}^tBu$, Ph or CH_2Ph), were prepared by the exchange reactions of $[WI_2(CO)_3$-

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[*] Corresponding author.

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$(NCMe)_2]$ with NCR [6]. The seven-coordinate complexes $[WI_2(CO)_3(NCR)_2]$ (R = Et, ^{t}Bu, Ph or CH_2Ph) when treated with an excess of but-2-yne or two equivalents of PhC_2Ph in CH_2Cl_2 at room temperature gave the bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ (R' = Me or Ph) (**1–8**) in good yield. All of the complexes **1–8** were fully characterised by elemental analysis (C, H and N) (Table 1) and by infrared (Table 2), ^{1}H NMR (Table 3) and, in selected cases, ^{13}C NMR spectroscopy (Table 4). The complex $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**3**) was also structurally characterised by X-ray crystallography. The complexes are all reasonably stable in the solid state when stored under nitrogen, but slowly decompose when exposed to air in solution. All the complexes **1–8** are soluble in chlorinated solvents, and slightly soluble in diethyl ether and hydrocarbon solvents. The bis(but-2-yne) complexes are much more soluble than their diphenylacetylene counterparts.

Complexes **1–8** all show a strong single carbonyl band in their IR spectra above 2000 cm^{-1}, with, as expected, the bis(diphenylacetylene) complexes having higher stretching frequences than their bis(but-2-yne) analogues. The weak asymmetric doublets at around 2300 cm^{-1} for the complexes can be ascribed to coordinated acetonitrile. The increase in ν(CN) upon coordination to the tungsten is likely to be due to the coupling of the C–N bond to N-metal stretching vibrations and to an increase in the C–N force constant, which implies that the acetonitrile is bonding as a pure σ-donor ligand [7]. The weak alkyne stretching bands at $\cong$ 1825 cm^{-1} are at considerably lower wavenumber

Table 2
Infrared data [a] for the Bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$

Complex	ν(C≡O) cm^{-1}	ν(C≡N) cm^{-1}	ν(C≡C) cm^{-1}
1	2066s	2293w	1820w
2	2093s	2341w	1835w
3	2065s	2285w	1829w
4	2092s	2290w	not observed
5	2067s	2272w	not observed
6	2083s	2258w	not observed
7	2064s	2301w	1825w
8	2092s	2297w	1876w
9	2056s	–	not observed
10	1936s	–	not observed

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

Table 1
Physical and analytical data for the Bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ and derivatives

Complex	Colour	Yield (%)	Analytical Data (found (calc.)%)
1 $[WI_2(CO)(NCEt)(\eta^2\text{-}MeC_2Me)_2]$	Yellow	45	C: 22.7 (22.9) H: 2.7 (2.7) N: 1.9 (2.2)
2 $[WI_2(CO)(NCEt)(\eta^2\text{-}PhC_2Ph)_2]$	Orange	38	C: 43.6 (43.8) H: 2.5 (2.8) N: 1.6 (1.6)
3 $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$	Yellow	40	C: 25.5 (25.6) H: 3.3 (3.2) N: 2.0 (2.1)
4 $[WI_2(CO)(NC^tBu)(\eta^2\text{-}PhC_2Ph)_2]$	Yellow	54	C: 45.4 (45.1) H: 3.2 (3.2) N: 1.6 (1.6)
5 $[WI_2(CO)(NCPh)(\eta^2\text{-}MeC_2Me)_2]$	Yellow	42	C: 28.1 (28.4) H: 2.6 (2.5) N: 1.8 (2.1)
6 $[WI_2(CO)(NCPh)(\eta^2\text{-}PhC_2Ph)_2]$	Yellow	30	C: 46.6 (46.7) H: 3.1 (2.7) N: 1.4 (1.5)
7 $[WI_2(CO)(NCCH_2Ph)(\eta^2\text{-}MeC_2Me)_2]$	Yellow	36	C: 29.8 (29.5) H: 2.8 (2.8) N: 2.1 (2.0)
8 $[WI_2(CO)(NCCH_2Ph)(\eta^2\text{-}PhC_2Ph)_2]$	Yellow	47	C: 47.3 (47.3) H: 3.1 (2.9) N: 2.1 (1.5)
9 $[WI(CO)(2,2'\text{-bipy})(\eta^2\text{-}MeC_2Me)_2]I$	Yellow	42	C: 31.2 (31.3) H: 2.8 (2.8) N: 3.7 (3.8)
10 $[WI_2(CO)(Ph_2P(CH_2)PPh_2)(\eta^2\text{-}MeC_2Me)]$	Green	34	C: 39.3 (39.8) H: 3.0 (3.1)

Table 3
^{1}H NMR Data [a] for the bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$

Complex	^{1}H (δ) ppm
1	3.20 (q, 2H, CH_3CH_2CN); 2.87 (s, 6H, MeC_2); 2.67 (s, 6H, MeC_2); 1.68 (t, 3H, CH_3CH_2CN)
2	7.50–7.30 (m, 20H, PhC_2); 2.68 (q, 2H, CH_3CH_2CN); 1.10 (t [illegible] H_3CH_2CN)
3	2.85 [illegible]H, MeC_2); 2.75 (s, 6H, MeC_2); 1.73 (s, 9H, Me_3CCN)
4	7.60–7.30 (brm, 20H, PhC_2); 1.24 (s, 9H, Me_3CCN)
5	8.15–7.46 (brm, 5H, $PhCN$); 2.90 (s, 6H, MeC_2); 2.87 (s, 6H, MeC_2)
6	7.73–7.30 (brm, PhC_2, $PhCN$)
7	7.68–7.29 (brm, 5H, $PhCH_2CN$); 4.56 (s, 2H, $PhCH_2CN$); 2.87 (s, 6H, MeC_2); 2.67 (s, 6H, MeC_2)
8	7.48–7.10 (brm, 25H, PhC_2, $-PhCH_2CN$); 4.09 (s, 2H, $PhCH_2CN$)
9	8.74 (d, 2H, *bipy*); 8.36 (t, 2H, *bipy*); 7.68 (m, 4H, *bipy*); 3.42 (s, 6H, MeC_2); 3.21 (s, 6H, MeC_2)
10	7.85–7.10 (brm, 20H, *Ph*); 4.80 (brm, 2H, CH_2P); 2.95 (s, 6H, MeC_2)

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$.
s = singlet; d = doublet; t = triplet; q = quartet; brm = broad multiplet.

than are those for the corresponding "free" ligand as determined by Raman spectroscopy. This must be due to the synergistic effect of back-donation of electron density from filled metal d-type orbitals into empty π^*-orbitals on the alkyne ligands.

The molecular structure of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**3**) is shown in Fig. 1, together with its atomic numbering scheme. The complex is formally eight-coordinate, but it is convenient to consider the geometry as six-coordinate, with the but-2-yne ligands occupying one coordination site each. The two iodo atoms are mutually *cis*-, and each is *trans*- to a but-2-yne moiety. The carbon monoxide ligand is *trans*- to the acetonitrile. The molecule has an approximate mirror plane of symmetry passing through the O(1), C(14), W(1), N(1), C(9), C(10) and C(13) atoms (maximum atomic deviation 0.067 Å) and relating the pairs of iodine atoms and MeC_2Me groups. It is also noted that the compound is a 50/50 racemic twin in the crystal.

The structure of **3** resembles very closely four other related structures in the series, i.e. $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}(\eta^2\text{-}MeC_2Me)_2]$ $\{NCCH_2(3\text{-}C_4H_3S)$ = thiophene-3-acetonitrile$\}$ (A) [9], $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (B) [5], $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (C) [5] and $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$ (D) [8], all of which have very similar ligand dispositions around the metal centre. The distances of I, acetylenic carbons, C(CO) and N(NCR) from W in **3** [2.894, 2.881(2) Å; 2.05–2.14(2) Å; 2.02(1) Å; 2.17(1) Å, respectively] are also similar to the corresponding values [2.858, 2.892(3) Å; 1.95–2.21(4) Å; 1.91(6) Å; 2.13(4) Å] in (A), [2.843, 2.859(1) Å; 2.03–2.12(2) Å; 1.94(2) Å; 2.13(2) Å] in (B), [2.848, 2.862(2) Å; 2.05–2.08(2) Å; 2.02(2) Å; 2.17(2) Å]

Table 4
Selected ^{13}C NMR Data [a] for the Bis(alkyne) complexes $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$

Complex	^{13}C (δ) ppm
1	206.99 (s, $C\equiv O$); 167.59 (s, $C\equiv C$, J_{W-C} = 16.25 Hz); 156.59 (s, $C\equiv C$, J_{W-C} = 7.67 Hz); 132.72 (s, $C\equiv N$); 19.75, 15.69 (2s, MeC_2); 13.32 (s, CH_3CH_2CN); 10.11 (s, CH_3CH_2CN)
2	201.35 (s, $C\equiv O$); 175.30 (s, $C\equiv C$, J_{W-C} = 16.11 Hz); 164.15 (s, $C\equiv C$, J_{W-C} = 9.32 Hz); 137.50–127.88 (brm, C–Ph); 133.25 (s, $C\equiv N$); 13.21 (s, CH_3CH_2CN); 8.97 (s, CH_3CH_2CN)
6	201.29 (s, $C\equiv O$, J_{W-C} = 48.99 Hz); 175.18 (s, $C\equiv C$, J_{W-C} = 16.06 Hz); 164.0 (s, $C\equiv C$, J_{W-C} = 8.84 Hz); 137.50–128.04 (brm, C–Ph, C–PhCN); 109.76 (s, $C\equiv N$)

[a] Spectra recorded in CD_2Cl_2 (+25°C) referenced to $SiMe_4$.
s = singlet; t = triplet; q = quartet; m = multiplet; br = broad.

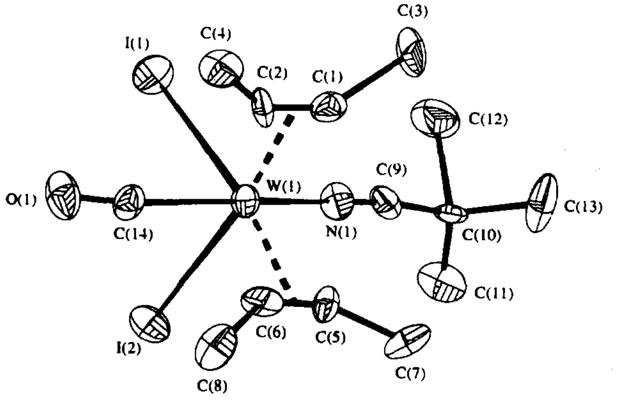

Fig. 1. X-ray structure of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**3**) showing the atom number scheme. The hydrogen atoms are omitted for clarity.

in (C) and [2.851, 2.862(1) Å; 2.06–2.12(2) Å; 2.07, 2.09(2) Å] in (D). The differences in the chemically equivalent bond distances are very small, and in view of the experimental uncertainties involved appear to be of marginal significance (if any, except for the W–I bond lengths). The W–(η^2-C≡C) bonds are most probably symmetrical. Other dimensions are as expected. The differences observed between the corresponding bond angles are also small, and probably result from steric factors and packing requirements of the molecules in the crystal.

The ^{1}H NMR data (Table 3) for (**1–8**) conform with the expected structure shown in Fig. 1. The bis(but-2-yne) complexes, as expected, show two resonances for the methyl groups on the but-2-yne ligands, i.e. one resonance for the methyl groups pointing to the carbonyl ligand and one for the methyl groups directed towards the nitrile ligand. Templeton and Ward [10] have correlated the number of electrons donated by an alkyne to a transition-metal centre with the ^{13}C NMR chemical shift for the alkyne contact carbon. The values for the alkyne contact carbon atoms obtained for complexes **1**, **2** and **6** are in the range 175.30–156.59 ppm which conforms with the alkynes donating a total of six-electrons to the tungsten. These observations are also in accord with the complexes obeying the effective atomic number rule.

The reactions of **3** are similar to those of the acetonitrile complex $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$. For example, equimolar quantities of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ and L^L {L^L = 2,2′-bipy or $Ph_2P(CH_2)PPh_2$} react in CH_2Cl_2 at room temperature to give $[WI(CO)(2,2'\text{-bipy})(\eta^2\text{-}MeC_2Me)_2]I$ (**9**) or $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ (**10**), respectively. Both of these complexes have been previously prepared and crystallographically characterised [11,12].

3. Experimental details

The compounds were synthesised by use of standard vacuum/Schlenk line techniques under dry nitrogen. All solvents were dried and purged with nitrogen before use. The starting materials $[WI_2(CO)_3(NCR)_2]$ (R = Et, ^{t}Bu, Ph or CH_2Ph) were prepared by treating $[WI_2(CO)_3(NCMe)_2]$ with an excess of NCR [6]. All other chemicals used were obtained from commercial sources and were used without purification.

Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. Elemental analyses (C, H and N) were carried out with a Carlo-Erba elemental analyser MOD 1106 (with helium as a carrier gas). The ^{1}H and ^{13}C NMR spectra were recorded respectively on Bruker AC 250 MHz (University of Wales, Bangor) and Bruker WH 400 MHz (University of Warwick) spectrometers.

3.2. *$[WI_2(CO)(NCEt)(\eta^2\text{-}PhC_2Ph)_2]$ (2)*

To a stirred solution of $[WI_2(CO)_3(NCEt)_2]$ (0.4 g, 0.633 mmol) in 15 ml of CH_2Cl_2 was added diphenylacetylene (0.23 g, 1.266 mmol). The solution was stirred for 20 h and then filtered. The solvent was removed in vacuo to leave an orange powder, which was re-dissolved in the minimum amount of CH_2Cl_2. A few drops of diethyl ether were added and the solution kept at −17°C for 24 h to give orange crystals of $[WI_2(CO)(NCEt)(\eta^2\text{-}PhC_2Ph)_2]$ (**2**) (Yield = 0.21 g, 38%).

Similar reactions of $[WI_2(CO)_3(NCR)_2]$ (where R = ^{t}Bu, Ph or CH_2Ph) with two equivalents of diphenylacetylene in CH_2Cl_2 at room temperature and subsequent recrystallisation from CH_2Cl_2/Et_2O and cooling the solution to −17°C yielded the analogous complexes $[WI_2(CO)(NCR)(\eta^2\text{-}PhC_2Ph)_2]$ **4**, **6** and **8** (for physical and analytical data see Table 1).

3.3. *$[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (3)*

To a continuously stirred solution of $[WI_2(CO)_3(NC^tBu)_2]$ (0.66 g, 0.96 mmol) in CH_2Cl_2 (15 ml) under a stream of dry nitrogen was added an excess of but-2-yne (0.21 g, 0.30 ml, 3.84 mmol). After 20 h stirring the solution was filtered, and the solvent was removed in vacuo to leave a yellow powder, which was redissolved in the minimum of CH_2Cl_2. A few drops of diethyl ether were added and the solution was cooled to −17°C and left for 24 h to give yellow crystals of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (**3**) suitable for X-ray crystallography (yield = 0.25 g, 40%).

Similar reactions of $[WI_2(CO)_3(NCR)_2]$ (where R = Et, Ph or CH_2Ph) with an excess of but-2-yne in CH_2Cl_2 at room temperature and subsequent recrystallisation from CH_2Cl_2/Et_2O at −17°C yielded the analogous complexes $[WI_2(CO)(NCR)(\eta^2\text{-}MeC_2Me)_2]$ **1**, **5** and **7** (for physical and analytical data see Table 1).

3.4. *$[WI(CO)(2,2'\text{-}bipy)(\eta^2\text{-}MeC_2Me_2)_2]I$ (9)*

To a stirred solution of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (0.20 g, 0.304 mmol) in 15 ml of CH_2Cl_2 was added 2,2′-bipyridyl (0.05 g, 0.304 mmol). The solution was stirred for 20 h then filtered. The solvent was removed in vacuo to produce a yellow powder, which was recrystallised from CH_2Cl_2 at −17°C to afford analytically pure $[WI(CO)(2,2'\text{-bipy})(\eta^2\text{-}MeC_2Me)_2]I$ (**9**) (yield = 0.09 g, 42%).

3.5. *$[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ (10)*

To a solution of $[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$ (0.20 g, 0.304 mmol) in 15 ml of CH_2Cl_2 with continuous stirring under a stream of dry nitrogen was added

$Ph_2P(CH_2)PPh_2$ (0.12 g, 0.304 mmol). After stirring for 20 h the solution was filtered. The solvent was removed in vacuo to produce a green powder, which was recrystallised from CH_2Cl_2 at −17°C to yield analytically pure $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ (**10**) (yield = 0.1 g, 34%).

3.6. *X-ray crystallography*

Crystals of **3** suitable for X-ray work were grown from 80/20 CH_2Cl_2/Et_2O at −17°C.

3.6.1. *Crystal data*

$[WI_2(CO)(NC^tBu)(\eta^2\text{-}MeC_2Me)_2]$, $C_{14}H_{21}I_2NOW$, M = 656.97, orthorhombic, $a = 11.449(1)$, $b = 13.000(1)$, $c = 13.229(2)$ Å, $U = 1969.0$ Å^3 (by least squares refinement of diffractometer angles for 250 reflections within $\theta = 2.5\text{–}29.7°$, $\lambda = 0.71069$ Å), space group $P2_12_12_1$, $Z = 4$, $D_c = 2.216$ g cm^{-3}, $F(000) = 1200$, $\mu = 90.0$ cm^{-1}, T = 293 K, crystal size 0.20 × 0.15 × 0.10 mm^3.

All crystallographic measurements were made on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo Kα radiation by following procedures described elsewhere [13], 7972 reflections were measured ($2.2 < \theta < 29.7°$; index ranges $-8 < h < 15$; $-11 < k < 16$; $-17 < l < 17$), which yielded 3936 unique data [merging $R = 0.0346$]. The data were corrected for absorption using the program DIFABS [14] (max. and min. absorption correction factors = 0.900, 1.091)].

Table 5
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $C_{14}H_{21}NOI_2W$

	x	y	z	U_{eq}
W(1)	4318(1)	4998(1)	9324(1)	28(1)
I(1)	2681(2)	6490(1)	8532(1)	45(1)
I(2)	2663(2)	3523(1)	8554(1)	44(1)
N(1)	4965(5)	5003(16)	7779(4)	40(2)
O(1)	2520(5)	5033(20)	11131(4)	55(2)
C(1)	5562(24)	6130(15)	9510(16)	37(5)
C(2)	4948(15)	6115(14)	10276(14)	34(5)
C(3)	6452(21)	6785(18)	8840(16)	58(6)
C(4)	4829(23)	6571(15)	11372(12)	46(5)
C(5)	5508(21)	3778(16)	9428(14)	30(4)
C(6)	4963(20)	3802(14)	10287(15)	37(6)
C(7)	6461(21)	3356(16)	8931(14)	48(5)
C(8)	4710(23)	3261(17)	11210(13)	50(5)
C(9)	5314(5)	5001(22)	6973(5)	35(2)
C(10)	5810(7)	4876(15)	5946(6)	29(3)
C(11)	5462(24)	4063(14)	5410(10)	51(5)
C(12)	5329(27)	6005(17)	5354(17)	73(7)
C(13)	7132(7)	5021(24)	6060(7)	71(4)
C(14)	3172(6)	4960(22)	10484(5)	36(2)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 6
Bond lengths (Å) and angles (deg) for $C_{14}H_{21}NOI_2W$

W(1)–I(1)	2.894(2)	W(1)–I(2)	2.881(2)
W(1)–C(1)	2.06(2)	W(1)–C(2)	2.05(2)
W(1)–C(5)	2.10(2)	W(1)–C(6)	2.14(2)
W(1)–C(14)	2.019(7)	W(1)–N(1)	2.173(5)
N(1)–C(9)	1.140(7)	O(1)–C(14)	1.140(8)
C(1)–C(2)	1.23(3)	C(1)–C(3)	1.60(3)
C(2)–C(4)	1.57(2)	C(5)–C(6)	1.30(3)
C(5)–C(7)	1.39(3)	C(6)–C(8)	1.44(3)
C(9)–C(10)	1.481(10)	C(10)–C(11)	1.33(2)
C(10)–C(13)	1.533(13)	C(10)–C(12)	1.75(3)
C(14)–W(1)–C(1)	112.0(9)	C(2)–W(1)–C(1)	34.9(8)
C(14)–W(1)–C(2)	77.2(7)	C(14)–W(1)–C(5)	110.7(8)
C(2)–W(1)–C(5)	105.4(8)	C(1)–W(1)–C(5)	94.8(4)
C(14)–W(1)–C(6)	75.8(8)	C(2)–W(1)–C(6)	91.5(3)
C(1)–W(1)–C(6)	102.0(9)	C(5)–W(1)–C(6)	35.6(8)
C(2)–W(1)–N(1)	117.1(7)	C(1)–W(1)–N(1)	82.8(7)
C(5)–W(1)–N(1)	80.9(7)	C(6)–W(1)–N(1)	116.4(8)
C(2)–W(1)–I(2)	156.7(5)	C(1)–W(1)–I(2)	166.2(6)
C(5)–W(1)–I(2)	87.0(6)	C(6)–W(1)–I(2)	87.4(6)
C(2)–W(1)–I(1)	88.6(6)	C(1)–W(1)–I(1)	90.7(6)
C(5)–W(1)–I(1)	162.3(5)	C(6)–W(1)–I(1)	157.7(6)
C(14)–W(1)–N(1)	159.4(3)	C(14)–W(1)–I(2)	79.9(6)
N(1)–W(1)–I(2)	83.9(3)	C(14)–W(1)–I(1)	82.5(5)
N(1)–W(1)–I(1)	83.0(4)	I(2)–W(1)–I(1)	83.80(2)
C(9)–N(1)–W(1)	179.3(13)	C(2)–C(1)–C(3)	146(2)
C(2)–C(1)–W(1)	72(2)	C(3)–C(1)–W(1)	139(2)
C(1)–C(2)–C(4)	143(2)	C(1)–C(2)–W(1)	73.0(14)
C(4)–C(2)–W(1)	143.3(14)	C(6)–C(5)–C(7)	144(2)
C(6)–C(5)–W(1)	74.2(12)	C(7)–C(5)–W(1)	141(2)
C(5)–C(6)–C(8)	146(2)	C(5)–C(6)–W(1)	70.2(12)
C(8)–C(6)–W(1)	142(2)	C(11)–C(10)–C(9)	117(2)
C(11)–C(10)–C(13)	116(2)	C(9)–C(10)–C(13)	106.0(7)
C(11)–C(10)–C(12)	109.4(8)	C(9)–C(10)–C(12)	101(2)
C(13)–C(10)–C(12)	105(2)	O(1)–C(14)–W(1)	174(3)
W(1)–C(01) [a]	1.96	W(1)–C(02) [a]	2.02
I(1)–W(1)–C(01) [a]	89.6	I(2)–W(1)–C(01) [a]	172.0
N(1)–W(1)–C(01) [a]	99.9	C(14)–W(1)–C(01) [a]	94.7
I(1)–W(1)–C(02) [a]	170.4	I(2)–W(1)–C(02) [a]	87.0
N(1)–W(1)–C(02) [a]	98.9	C(14)–W(1)–C(02) [a]	93.1
C(01)–W(1)–C(02) [a]	99.3		

[a] C(01) and C(02) denote the centres of the C(1)=C(2) and C(5)=C(6) double bonds respectively.

The structure was solved via direct methods (W and I atoms) (SHELX-S) [15] followed by normal heavy atom procedures. Full-matrix least squares refinement of F^2 (SHELXL-93) [16] with all non-hydrogen atoms anisotropic and hydrogen atoms in idealised positions with U_{iso}'s set at 1.5 times the U_{eq}'s of the parent carbons gave final $wR_2(=[\Sigma\{w(\Delta(F^2)^2)\}/\Sigma\{w(F_o^2)^2\}]^{1/2}) = 0.073$ and $R_1[=\Sigma(|\Delta F|)/\Sigma(F_o)] = 0.031$ for all 3936 data and 180 parameters. The corresponding R indices for 3262 reflections with $I > 2\sigma(I)$ were 0.067 and 0.027 respectively. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$. The use of SHELXL-93 [16] for refinement indicated that the structure was a possible racemic twin. This was dealt with by applying the racemic twin matrix TWIN −1 0 0 0 −1 0 0 0 −1 2 and refining a BASF scale factor; with the final BASF value o 0.50(3), it showed an ideal example of racemic twinning. The calculations were performed on a

486DX2/66 personal computer. Sources of scattering factor data are given in Ref. [16].

The fractional coordinates of the non-hydrogen atoms and bond lengths and angles are given in Tables 5 and 6 respectively. The hydrogen atom parameters, anisotropic displacement parameters of the non-hydrogen atoms, and tables of structure factors have been deposited as supplementary materials.

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References

[1] A. Efraty, *Chem. Rev., 77* (1977) 691.
[2] D.P. Tate and J.M. Augl, *J. Am. Chem. Soc., 85* (1963) 2174.
[3] M. Bottrill and M. Green, *J. Chem. Soc., Dalton Trans.,* (1977) 2365.
[4] J.L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.,* (1985) 2239.
[5] E.M. Armstrong, P.K. Baker and M.G.B. Drew, *Organometallics, 7* (1988) 319.
[6] P.K. Baker, M.E. Harman, M.B. Hursthouse, A.I. Karaulov, A.J. Lavery, K.M. Abdul Malik, D.J. Muldoon and A. Shawcross, submitted to *Inorg. Chem.*
[7] P.C. Ford and R.E. Clarke, *J. Chem. Soc., Chem. Commun.,* (1968) 1109.
[8] E.M. Armstrong, P.K. Baker and M.G.B. Drew, *J. Organomet. Chem., 336* (1987) 377.
[9] P.K. Baker, M.G.B. Drew, S. Edge and S.D. Ridyard, *J. Organomet. Chem., 409* (1991) 207.
[10] J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc., 102* (1980) 3288.
[11] P.K. Baker, E.M. Armstrong and M.G.B. Drew, *Inorg. Chem., 27* (1988) 2287.
[12] E.M. Armstrong, P.K. Baker, M.E. Harman and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* (1989) 295.
[13] J.A. Darr, S.R. Drake, M.B. Hursthouse and K.M.A. Malik, *Inorg. Chem., 32* (1993) 5704.
[14] N.P.C. Walker and D. Stuart, *Acta Crystallogr., A39* (1983) 158.
[15] G.M. Sheldrick, *Acta Crystallogr., A46* (1990) 467.
[16] G.M. Sheldrick, University of Göttingen, Germany, 1993.