Acetonitrile exchange reactions of [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) and [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] with thiophene-3-acetonitrile. X-Ray crystal structure of [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}(η^2-MeC$_2$Me)$_2$]

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Abstract

The complexes [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) and [WI(CO)(NCMe)(Ph$_2$P(CH$_2$)-PPh$_2$)(η^2-MeC$_2$Me)][BF$_4$] react with equimolar quantities of thiophene-3-acetonitrile (NCCH$_2$(3-C$_4$H$_3$S)) in dichloromethane at room temperature to give the acetonitrile-exchanged products [WI$_2$(CO)-{NCCH$_2$(3-C$_4$H$_3$S)}(η^2-RC$_2$R)$_2$] (**1** and **2**) and [WI(CO){NCCH$_2$(3-C$_4$H$_3$S)}{Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] (**3**) respectively in good yields. The crystal structure of [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}-(η^2-MeC$_2$Me)$_2$] (**1**) was determined. The coordination geometry about the tungsten may be regarded as octahedral, with the but-2-yne ligands parallel to each other and *trans* to the iodide ligands. The carbon monoxide and thiophene-3-acetonitrile ligands are mutually *trans* to each other. ^{13}C NMR spectroscopy indicates that the alkyne ligands in **1** are donating a total of six electrons to the tungsten, whereas the but-2-yne ligand in **3** is donating four electrons to the tungsten. The barrier to but-2-yne rotation of **3** was calculated to be 51.3 kJ mol^{-1}.

Introduction

The polymerisation of thiophene and substituted thiophene derivatives has received considerable attention in recent years [1–4], in order to synthesize linear conducting polymers. In order to incorporate thiophene into an organometallic redox centre we utilise thiophene-3-acetonitrile to coordinate to organotransition-metal tungsten centres via the nitrile group. In this paper we describe the reactions of [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) and [WI(CO)(NCMe){Ph$_2$P-(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] with thiophene-3-acetonitrile {NCCH$_2$(3-C$_4$H$_3$S)} to give the first examples of transition-metal complexes containing any thiophene derivative as a ligand attached through the nitrile group, namely [WI$_2$(CO)-{NCCH$_2$(3-C$_4$H$_3$S)}(η^2-RC$_2$R)$_2$] (**1** and **2**) and [WI(CO){NCHH$_2$(3-C$_3$H$_4$S)}{Ph$_2$-

P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] (3). The X-ray crystal structure of [WI$_2$(CO)-{NCCH$_2$(3-C$_3$H$_4$S)}(η^2-MeC$_2$Me)$_2$] (1) is also described.

Results and discussion

The starting materials [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) [5] and [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] [6] used for the research described in this paper were prepared by literature methods. Equimolar quantities of [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) and thiophene-3-acetonitrile {NCCH$_2$(3-C$_4$H$_3$S)} react in CH$_2$Cl$_2$ at room temperature to afford the complexes [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}(η^2-RC$_2$R)$_2$] (1 and 2) in good yield. The complex [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] reacts with an equimolar quantity of NCCH$_2$(3-C$_4$H$_3$S) to give [WI(CO){NCCH$_2$(3-C$_3$H$_4$S)}{Ph$_2$P(CH$_2$-PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] (3) in high yield. Complexes 1–3 were fully characterised by elemental analysis (C, H and N), IR spectroscopy, ^{1}H and in selected cases ^{13}C NMR spectroscopy (see Experimental). Compounds 1–3 are all soluble in OCMe$_2$, CH$_2$Cl$_2$, CHCl$_3$ and NCMe, but insoluble in Et$_2$O and hydrocarbon solvents. The complexes are stable in the solid state when stored under nitrogen for several weeks, however they slowly decompose when exposed to air, and much more rapidly decompose when exposed to air in solution.

The structure of [WI$_2$(CO){NCCH$_2$(3-C$_3$H$_4$S)}(η^2-MeC$_2$Me)$_2$] (1) has been determined by X-ray crystallography. The structure consists of discrete molecules of [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}(η^2-MeC$_2$Me)$_2$] illustrated in Fig. 1 together with the atomic numbering scheme. The tungsten atom is best described as six coordinate, with the two but-2-yne ligands each taking up one coordination site. The two ligands are both *trans* to an iodide ligand (W(1)–I(1) 2.892(3), W(1)–I(2) 2.858(3) Å). The coordination sphere is completed by carbon monoxide (W(1)–C(1) 1.91(6) Å) and thiophene-3-acetonitrile ligands (W–N(11) 2.13(4) Å) which are mutually *trans*. The W–C(but-2-yne) distances are equivalent within experimental error (W(1)–C(62) 1.95(4), W(1)–C(63) 2.18(5), W(1)–C(42) 2.19(3), W(1)–C(43) 2.21(4) Å).

The dimensions in the molecule are as expected. The disposition of the two alkynes is parallel as is apparent from Fig. 1; thus, the four central carbon atoms C(62), C(63), C(42), C(43) are planar within experimental error. The equatorial plane containing atoms I(1) and I(2) and the midpoints of the two but-2-yne ligands is also planar within experimental error with the tungsten atom 0.08 Å from the plane in the direction of N(11).

In the thiophene-3-acetonitrile ligand, the W(1)–N(11)–C(12)–C(13)–C(14) section is approximately planar (maximum deviation of a contributing atom 0.10 Å).

The infrared spectra of 1–3 all show a single carbonyl band in a similar region to their acetonitrile analogues. The IR spectra of 1–3 also show weak ν(C≡C) stretching bands at much lower wavenumber compared to the free alkyne, which suggests weakening of the alkyne bond strength due to back donation of electron density from filled metal d_π-orbitals into empty π^*-orbitals on the alkyne. Figure 1 shows the but-2-yne methyl groups on the coordinated alkynes are bent back which also suggests rehybridisation of the alkyne triple bond. A strong broad band at ≈ 1050 cm^{-1} due to ν(BF) stretching band [7] for complex 3 confirms the cationic nature of this compound.

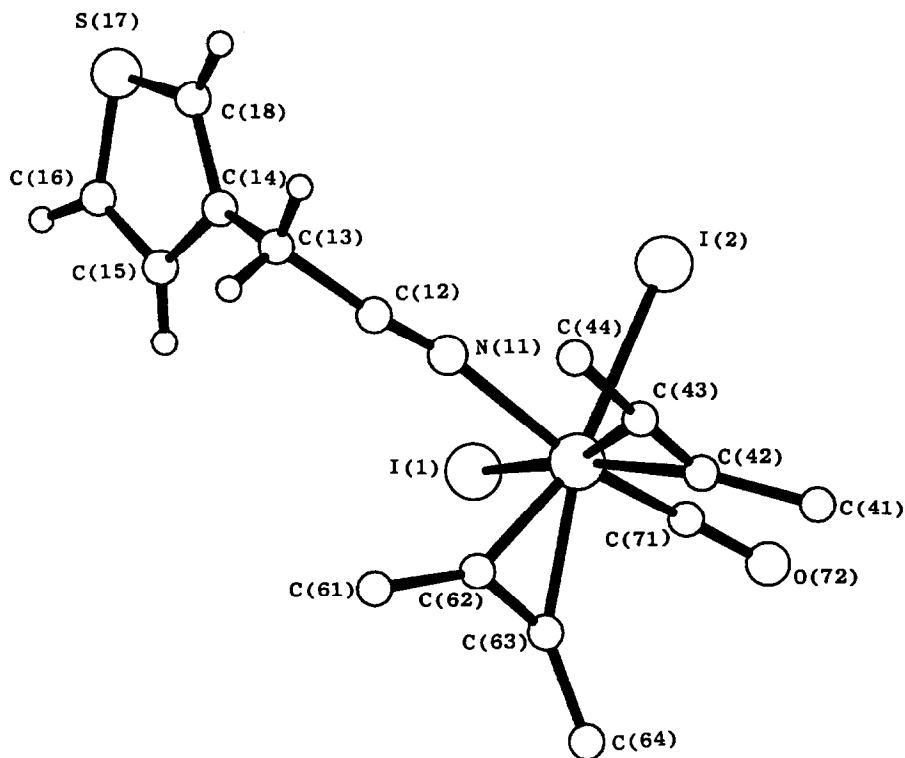Fig. 1. X-Ray crystal structure of $[WI_2(CO)\{NCCH_2(3-C_4H_3S)\}(\eta^2-MeC_2Me)_2]$ (1).

The ^{1}H NMR spectra of 1–3 all show the expected resonances for the coordinated thiophene-3-acetonitrile. Variable temperature ^{1}H NMR studies were carried out on the mono(but-2-yne) complex 3 which allowed the barrier to but-2-yne rotation to be calculated by using the equation $\Delta G^* = -RT_c\ln(\pi\Delta\nu/\sqrt{2}\,K_BT_c)$ ($T_c = 247$ K, $\Delta\nu = 32.11$ Hz) [8,9] and was calculated to be 51.3 kJ mol^{-1}. This is lower than the analogous triisopropylphosphite complex $[WI(CO)\{P(O^iPr)_3\}\{Ph_2P-(CH_2)PPh_2\}(\eta^2-MeC_2Me)][BF_4]$ which has $\Delta G^* = 56.9$ kJ mol^{-1} [6].

The but-2-yne ligands in complex 1 have ^{13}C NMR alkyne contact carbon resonances at $\delta = 156.40$ and 166.94 ppm which suggests [10] that the two but-2-yne ligands are donating a total of six electrons to the tungsten in this compound. The ^{13}C NMR spectrum of 3 has alkyne contact carbon resonances at $\delta = 206.36$ ppm which indicates [10] the but-2-yne is utilising both its filled p_π-orbitals and donating four electrons to the tungsten.

We are currently studying the electrochemical properties of complexes 1–3.

Experimental

The synthesis, purification and reactions of all complexes described were carried out under an atmosphere of nitrogen using standard Schlenk-line techniques. The compounds $[WI_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ (R = Me or Ph) [5] and [WI(CO)-

(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] [6] were prepared by the published methods. All other chemicals were purchased from commercial sources. The solvent, CH$_2$Cl$_2$ was distilled over P$_4$O$_{10}$ before use.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental analyser MOD 1106, using helium carrier gas. IR spectra were recorded on a Perkin–Elmer 1430 ratio recording infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker WH 400 NMR spectrometer or a Bruker AC 250 CP/MAS NMR spectrometer, all spectra were calibrated against tetramethylsilane.

[WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}(η^2-MeC$_2$Me)$_2$] (1)

To [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (0.5 g, 0.813 mmol) dissolved in CH$_2$Cl$_2$ (20 cm^3) was added NCCH$_2$(3-C$_4$H$_3$S) (0.10 g, 0.813 mmol) with continuous stirring under a stream of nitrogen for 18 h. Removal of the solvent *in vacuo* gave a dirty brown oil which, when washed with dry Et$_2$O (40 cm^3), gave a yellow powder [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}(η^2-MeC$_2$Me)$_2$] (1) which was recrystallised from CH$_2$Cl$_2$/Et$_2$O; yield of pure product 0.29 g, 51%. A suitable single crystal for X-ray crystallography was obtained by dissolving 0.29 g of [WI$_2$(CO){NCCH$_2$(3-C$_4$H$_3$S)}-(η^2-MeC$_2$Me)$_2$] (1) in the minimum volume (2 cm^3) of CHCl$_3$, followed by carefully adding a layer of 40–60 petroleum ether above the CHCl$_3$ layer and leaving under nitrogen in a Schlenk tube for several days at room temperature.

Data for 1: Analysis. Found: C, 25.9; H, 2.8; N, 1.9; C$_{15}$H$_{17}$NOSI$_2$W calc: C, 25.9; H, 2.5; N, 2.0%. IR (CH$_2$Cl$_2$) ν(N≡C) 2380w and 2420w, ν(C≡O) 2050s, ν(C≡C) 1830w cm^{-1}. NMR (ppm, CDCl$_3$, +25°C), ^{1}H, δ 7.1 (d), 7.3 (m), 7.5 (m)

Table 1

Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
W(1)	9033(1)	3040(3)	3596(1)
I(1)	9084(1)	1218(5)	4878(1)
I(2)	8091(1)	1156(5)	3427(1)
N(11)	8529(12)	4811(56)	4105(16)
C(12)	8339(13)	5872(58)	4381(16)
C(13)	8014(13)	7274(58)	4746(17)
C(14)	7831(13)	6504(53)	5381(17)
C(15)	8115(18)	5895(75)	6003(24)
C(16)	7782(23)	5829(93)	6494(33)
S(17)	7183(7)	5874(24)	6328(8)
C(18)	7307(14)	6483(56)	5584(19)
C(71)	9308(20)	776(90)	3376(26)
O(72)	9523(14)	9674(62)	3045(19)
C(61)	9649(16)	6231(73)	4295(22)
C(62)	9563(13)	4609(58)	3942(16)
C(63)	9854(18)	3345(72)	3767(22)
C(64)	10373(18)	2800(72)	3604(22)
C(41)	9238(16)	2623(74)	1868(23)
C(42)	9086(12)	3549(43)	2511(13)
C(43)	8829(16)	4598(67)	2690(19)
C(44)	8539(17)	6314(70)	2728(22)

Table 2

Molecular dimensions in the coordination sphere, distances (Å) and angles (°)

W(1)–I(1)	2.892(3)	W(1)–C(62)	1.95(4)
W(1)–I(2)	2.858(3)	W(1)–C(63)	2.18(5)
W(1)–N(11)	2.13(4)	W(1)–C(42)	2.19(3)
W(1)–C(71)	1.91(6)	W(1)–C(43)	2.21(4)
I(1)–W(1)–I(2)	84.47(10)	C(62)–W(1)–C(63)	35.3(16)
I(1)–W(1)–N(11)	85.2(9)	I(1)–W(1)–C(42)	160.6(8)
I(2)–W(1)–N(11)	80.9(9)	I(2)–W(1)–C(42)	91.6(8)
I(1)–W(1)–C(71)	75.7(15)	N(11)–W(1)–C(42)	113.1(12)
I(2)–W(1)–C(71)	81.1(15)	C(71)–W(1)–C(42)	84.9(17)
N(11)–W(1)–C(71)	154.9(18)	C(62)–W(1)–C(42)	101.1(12)
I(1)–W(1)–C(62)	87.2(10)	C(63)–W(1)–C(42)	94.1(14)
I(2)–W(1)–C(62)	162.8(10)	I(1)–W(1)–C(43)	167.8(11)
N(11)–W(1)–C(62)	83.4(14)	I(2)–W(1)–C(43)	88.1(11)
C(71)–W(1)–C(62)	111.3(19)	N(11)–W(1)–C(43)	84.1(15)
I(1)–W(1)–C(63)	82.5(12)	C(71)–W(1)–C(43)	112.7(19)
I(2)–W(1)–C(63)	156.1(14)	C(62)–W(1)–C(43)	97.4(16)
N(11)–W(1)–C(63)	117.7(15)	C(63)–W(1)–C(43)	107.8(16)
C(71)–W(1)–C(63)	76.2(20)	C(42)–W(1)–C(43)	28.9(12)

(3H, C_4H_3S); 3.85 (s, 2H, $NCCH_2$); 2.7, 2.9 (2 × s, 12H, $\equiv CMe$). ^{13}C, δ 205 (s, $C\equiv O$); 166.94 (s, $C\equiv C$); 156.40 (s, $C\equiv C$); 129.40, 127.22, 127.01 and 123.15 (4 × s, C_4H_3S); 118.0 (s, $N\equiv C$); 77.5 (s, $NCCH_2$) and 18.82 (s, MeC_2).

A similar reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with an equimolar quantity of $NCCH_2(3\text{-}C_4H_3S)$ gives the yellow complex $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}(\eta^2\text{-}PhC_2Ph)_2]$ (2), yield of pure product 56%.

Data for 2: Analysis. Found: C, 44.0; H, 3.0; N, 1.4. $C_{35}H_{25}NOSI_2W$ calc: C, 44.4; H, 2.7; N, 1.5%. IR (CH_2Cl_2) $\nu(N\equiv C)$ 2390w and 2430w, $\nu(C\equiv O)$ 2060s, $\nu(C\equiv C)$ 1840w cm^{-1}; NMR (ppm, CDCl$_3$, +25°C); ^1H, δ 7.45, 7.35 (m, 3H, C_4H_3S); 7.25 (m, 2OH); 3.75 (s, 2H, $NCCH_2$).

$[WI(CO)\{NCCH_2(3\text{-}C_4H_3S)\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (3)

To $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (0.3 g, 0.331 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of nitrogen, was added $NCCH_2(3\text{-}C_4H_3S)$ (0.05 g, 0.331 mmol). After stirring for 18 h the solvent was removed *in vacuo* giving the purple complex $[WI(CO)\{NCCH_2(3\text{-}C_4H_3S)\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (3), which was recrystallised from CH_2Cl_2/Et_2O; yield of pure product 0.33 g, 36%.

Data for 3: Analysis. Found: C, 43.8; H, 3.5; N, 1.2. $C_{36}H_{33}NOSIWBF_4$ calc: C, 43.8; H, 3.4; N, 1.4%. IR (CH_2Cl_2) $\nu(N\equiv C)$ 2359w, d, $\nu(C\equiv O)$ 1955s, $\nu(C\equiv C)$ 1791w cm^{-1}; NMR (ppm, CDCl$_3$, +25°C) ^1H, δ 7.3, 7.4, 7.6 (m, 23H, Ph + C_4H_3S), 5.1 (m, 2H, $P(CH_2)$), 3.72 (brs, 2H, $NCCH_2$), 3.1, 2.5 (2 × s, 6H, $\equiv CMe$), ^{13}C *, δ 206.36 (s, $C\equiv C$), 205.73 (s, $C\equiv O$), 123.24 (s, $N\equiv C$), (133.8 (s), 129.07 (d), 128.72 (d), 128.38 (d), 128.17 (d), 123.65 (s) {Ph + (C_4H_3S)}, 18.28 (s, Me).

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* No $NCCH_2$ carbon resonance was observed since it was obscured by the CDCl$_3$ resonance.

Crystal data for 1

Crystals were prepared as described above; $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}(\eta^2\text{-}MeC_2Me)_2]$, $C_{15}H_{17}NOSI_2W$, $M = 696.8$, orthorhombic, a 26.04(3), b 7.586(8), c 19.78(2) Å, U 3907 Å^3, D_c 2.37 g cm^{-3}, $D_m = 2.32$ g cm^{-3}, $F(000) = 2544$, $Z = 8$, λ 0.7107 Å, μ 95.5 cm^{-1}, space group *Pbca*.

A crystal of approximate size $0.3 \times 0.25 \times 0.25$ mm was set up to rotate about the c 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^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 3867 independent reflections were measured of which 1343 with $I > 3\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied [11]. The structure was determined by the heavy-atom method. The W, I and S atoms were refined anisotropically, C, N and O atoms isotropically. The methyl-hydrogen atoms could not be located but the remaining hydrogen atoms were included in calculated positions.

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.076 ($R_w = 0.083$). Calculations were carried out using SHELX76 [12] and some of our own programmes on the Amdahl 5870 at the University of Reading. Positional parameters are given in Table 1 and molecular dimensions in the tungsten coordination sphere are given in Table 2.

Acknowledgements

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