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Nitrile exchange reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W). X-ray crystal structures of the mixed-ligand seven-coordinate complexes $[WI_2(CO)_3(NCR)(AsPh_3)]$ (R = Et or Ph)

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Abstract

Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an excess of NCR (for M = W, R = Et, ^{t}Bu, CH_2Ph or Ph; for M = Mo, R = Ph) in CH_2Cl_2 at room temperature gives the nitrile-exchanged products $[MI_2(CO)_3(NCR)_2]$ (**1–5**). Equimolar quantities of **1–5** and L (L = PPh_3, $AsPh_3$ or $SbPh_3$) react in CH_2Cl_2 at room temperature to afford the mixed ligand complexes $[MI_2(CO)_3(NCR)L]$ (**6–20**). X-ray single crystallographic studies were carried out on both the tungsten complexes $[WI_2(CO)_3(NCR)(AsPh_3)]$ (R = Et and Ph). The metal atoms in both complexes have the same seven-coordinate, slightly distorted monocapped trigonal prismatic, coordination geometry, with very similar ligand dispositions. Low temperature ^{13}C NMR spectroscopy was used to correlate the solution and solid-state structures of several of these seven-coordinate complexes. The reactions of the bis(propionitrile) complex $[WI_2(CO)_3(NCEt)_2]$ with neutral monodentate donor ligands are also described.

Keywords: Molybdenum; Tungsten; Carbonyls; Nitrile; Crystal structure

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1. Introduction

Since the first seven-coordinate complexes of molybdenum(II) and tungsten(II), namely $[MoX_2(CO)_3(diars)]$ (X = Br or I; diars = 1,2-$Me_2AsC_6H_4AsMe_2$) were reported by Nigam et al. in 1960 [1], the importance of such species has been highlighted by their ability to act as alkene metathesis catalysts. Bencze and Kraut-Vass [2] have shown that the complexes $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) are single component catalysts at 80°C in benzene for the ring-opening polymerisation of norbornene and norbornadiene. Although a large number of seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$ have been reported [3–14], far fewer mixed ligand complexes of the type $[MX_2(CO)_3LL']$ have been described, reports being largly confined to the work of Umland and Vahrenkamp [15] and ourselves [16,17].

In 1986 [18], we described the oxidation of the zero-valent molybdenum and tungsten complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared in situ) with an equimolar amount of I_2 at 0°C to give the seven-coordinate bis(acetonitrile) complexes $[MI_2(CO)_3(NCMe)_2]$ in quantitative yield. In this paper we describe the nitrile exchange reactions of $[MI_2(CO)_3(NCMe)_2]$, and also the reactions of $[MI_2(CO)_3(NCR)_2]$ (for M = W, R = Et, ^{t}Bu, CH_2Ph or Ph; for M = Mo, R = Ph), with an equimolar quantity of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) to give $[MI_2(CO)_3(NCR)L]$. The molecular structures of the new mixed ligand complexes $[WI_2(CO)_3(NCR)(AsPh_3)]$(R = Et or Ph) are also described.

2. Results and discussion

The reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an excess of NCR (for M = W, R = Et, ^{t}Bu, CH_2Ph or Ph; for M = Mo, R = Ph) in CH_2Cl_2 at room

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temperature affords the nitrile-exchanged seven-coordinate complexes $[MI_2(CO)_3(NCR)_2]$ (**1–5**) in high yield. The complexes **1–5** have been characterised by elemental analysis (C, H and N) (Table 1), and by infrared (Table 2), ^{1}H NMR (Table 3), and, for R = CH_2Ph, by low temperature ^{13}C NMR spectroscopy (Table 4). The tungsten complexes are considerably more stable than their molybdenum analogues, hence only the bis(benzonitrile) complex was isolated and characterised for molybdenum, even though the other nitriles, NCR (R = Et, ^{t}Bu or CH_2Ph) were also treated with $[MoI_2(CO)_3(NCMe)_2]$. It was found that although reactions occurred with the molybdenum complexes, the final products $[MoI_2(CO)_3(NCR)_2]$ were very unstable and difficult to isolate in a pure state. It may be that the more labile molybdenum bis(nitrile) complexes dimerise rapidly to give $[Mo(\mu\text{-}I)I(CO)_3(NCR)]_2$. Some evidence to support this proposal comes from the reaction of $[MoI_2(CO)_3(NCMe)_2]$ with an excess of NC^{t}Bu in CH_2Cl_2 at room temperature for 30 min, which gives a

Table 1
Physical and analytical data for the seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes

Complex		Colour	Yield (%)	Analytical data (found (calc.) (%))		
				C	H	N
1	$[WI_2(CO)_3(NCEt)_2]$	Brown	77	16.6	1.5	4.2
				(17.1)	(1.6)	(4.4)
2	$[WI_2(CO)_3(NCBu^t)_2]$	Brown	81	22.6	2.6	3.6
				(22.7)	(2.6)	(4.1)
3	$[WI_2(CO)_3(NCCH_2Ph)_2]$	Black	83	30.4	1.9	3.8
				(30.2)	(1.9)	(3.7)
4	$[WI_2(CO)_3(NCPh)_2]$	Brown	65	27.5	1.4	3.8
				(28.0)	(1.4)	(3.8)
5	$[MoI_2(CO)_3(NCPh)_2]$	Black	72	31.4	1.7	4.6
				(31.9)	(1.6)	(4.4)
6	$[WI_2(CO)_3(NCEt)(PPh_3)]$	Yellow	63	34.5	2.5	2.4
				(34.3)	(2.4)	(1.7)
7	$[WI_2(CO)_3(NCEt)(AsPh_3)]$	Orange	56	32.6	2.2	1.5
				(32.6)	(2.3)	(1.6)
8	$[WI_2(CO)_3(NCEt)(SbPh_3)]$	Orange	54	31.1	2.3	1.9
				(31.0)	(2.2)	(1.5)
9	$[WI_2(CO)_3(NCBu^t)(PPh_3)]$	Yellow	66	35.6	2.8	1.3
				(36.0)	(2.8)	(1.6)
10	$[WI_2(CO)_3(NCBu^t)(AsPh_3)]$	Yellow	63	34.1	2.7	1.2
				(34.3)	(2.6)	(1.5)
11	$[WI_2(CO)_3(NCBu^t)(SbPh_3)]$	Yellow	38	33.8	2.7	1.0
				(33.8)	(2.5)	(1.5)
12	$[WI_2(CO)_3(NCCH_2Ph)(PPh_3)]$	Yellow	50	38.6	2.4	1.6
				(38.6)	(2.7)	(2.0)
13	$[WI_2(CO)_3(NCCH_2Ph)(AsPh_3)]$	Orange	47	36.7	2.5	2.1
				(36.8)	(2.3)	(1.5)
14	$[WI_2(CO)_3(NCCH_2Ph)(SbPh_3)]$	Yellow	46	35.7	2.5	2.0
				(35.1)	(2.2)	(1.4)
15	$[WI_2(CO)_3(NCPh)(PPh_3)]$	Yellow	46	37.7	2.6	1.5
				(37.9)	(2.3)	(1.6)
16	$[WI_2(CO)_3(NCPh)(AsPh_3)]$	Orange	66	36.6	2.2	1.7
				(36.1)	(2.2)	(1.5)
17	$[WI_2(CO)_3(NCPh)(SbPh_3)]$	Mustard	78	34.5	2.1	1.5
				(34.4)	(2.1)	(1.4)
18	$[MoI_2(CO)_3(NCPh)(PPh_3)]$	Brown	60	40.4	2.7	1.7
				(42.0)	(2.5)	(1.7)
19	$[MoI_2(CO)_3(NCPh)(AsPh_3)]$	Brown	43	39.4	2.6	1.8
				(39.8)	(2.4)	(1.7)
20	$[MoI_2(CO)_3(NCPh)(SbPh_3)]$	Pale Brown	43	37.1	2.5	3.3
				(37.8)	(2.3)	(1.6)
21	$[WI_2(CO)_3(PPh_3)(AsPh_3)]$	Yellow	37	43.5	2.8	0.0
				(42.9)	(2.8)	(0.0)
22	$[WI_2(CO)_3(AsPh_3)_2]$	Yellow	32	41.3	2.7	0.0
				(41.3)	(2.7)	(0.0)
23	$[WI_2(CO)_3(PPh_3)_2]$	Yellow	39	44.0	2.9	0.0
				(44.7)	(2.9)	(0.0)

Table 2
Infrared data [a] for the seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes

Complex	ν(C≡O)(cm^{-1})	ν(N≡C)(cm^{-1})
1	2073w, 2038s, 1913s	2287w, 2248w
2	2076w, 2027s, 1943s	2276w, 2234w
3	2075s, 2029s, 1946s	2273m
4	2073w, 2027s, 1947s	2263m, 2231w
5	2075s, 2035s, 1963s	2243w, sh
6	2031s, 1964s, 1913s	2281w
7	2028s, 1944s, 1914s	2288w
8	2033s, 1947s, 1907s	Not observed
9	2030s, 1963s, 1938s	2269w
10	2030s, 1965m, 1914m	2267w
11	2032s, 1965s, 1908s	2264w
12	2021s, 1957s, 1909s	2288w
13	2022s, 1959s, 1910s	2288w
14	2022s, 1962s, 1900s	2274w
15 [b]	2030s, 1961s, 1906s	2246m
16 [b]	2032s, 1962s, 1906s	2248w
17	2031s, 1967s, 1948s 1910s	2247w
18	2011m, 1935s, 1902s	2230w
19	2030s, 1968s, 1919m	2241w
20	2023w, 1942s, 1856s	2244w
21	2016s, 1944s, 1912s	–
22	2007s, 1939s, 1898s	–
23	2016s, 1944s, 1910s	–

[a] Spectra were recorded as thin films in $CHCl_3$ between NaCl plates except

[b] which were recorded as KBr discs.

complex that appears to be the iodo-bridged dimer $[Mo(\mu\text{-}I)I(CO)_3(NC^tBu)]_2$ as indicated by elemental analysis (C, H and N) and infrared and ^{1}H NMR spectroscopic data (see Experimental section 3.2). It should also be noted that stirring a solution of $[WI_2(CO)_3(NCR)_2]$ (**1–4**) in CH_2Cl_2 at room temperature for 24 h gave only the unchanged starting materials with no evidence of dimerisation. All the complexes **1–5** are air-sensitive in solution, but they can be stored under nitrogen in the solid state for long periods. The complexes are all soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. The aromatic nitrile complexes are more soluble than their aliphatic nitrile analogues.

The IR spectra for complexes **1–5** in $CHCl_3$ all have three carbonyl-stretching bands between 2076 cm^{-1} and 1913 cm^{-1}. These are similar to those in the IR spectra of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) which give three carbonyl bands between 2040 cm^{-1} and 1940 cm^{-1} in the same solvent. Complexes **1–5** also exhibit weak doublets at ca. 2300 cm^{-1} which are caused by the coordinated nitrile ligands. The coordination of NCR to the metal leads to an increase in the ν(NC) frequency compared with that for "free" ligand owing to coupling of the C≡N band to the N–metal stretching vibrations and to an increase in the C≡N force constant. This suggests that the nitrile is acting as a pure σ-donor ligand in these complexes [19]. The reactions of

Table 3
^{1}H NMR spectral data [a] for the seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes

Complex	^{1}H (δ)
1	2.85 (q, *J* = 14.29 Hz, 4H, NCC*H*$_2$CH$_3$); 1.42 (t, *J* = 7.14 Hz, 6H, NCCH$_2$C*H*$_3$)
2	1.11 (s, NCC*Me*$_3$)
3	7.86 (m, 10H, NCCH$_2$Ph-*H*); 4.17 (s, 4H, NCC*H*$_2$Ph)
4	7.90–7.41 (brm, NCPh-*H*)
5	7.60–7.44 (brm, NCPh-*H*)
6	7.91–7.41 (brm, 15H, Ph-*H*); 2.36 (q, *J* = 7.86 Hz, 2H, NCC*H*$_2$CH$_3$); 1.27 (t, *J* = 10.00 Hz, 3H, NCCH$_2$C*H*$_3$)
7	7.47 (m, 15H, Ph-*H*); 2.26 (q, *J* = 8.57 Hz, 2H, NCC*H*$_2$CH$_3$); 1.00 (t, *J* = 8.57 Hz, 3H, NCCH$_2$C*H*$_3$)
8	7.63–7.41 (brm, 15H, Ph-*H*); 2.35 (q, *J* = 7.14 Hz, 2H, NCC*H*$_2$CH$_3$); 1.26 (t, *J* = 5.00 Hz, 3H, NCCH$_2$C*H*$_3$)
9	7.44 (m, 15H, Ph-*H*); 1.11 (s, 9H, NCC*Me*$_3$)
10	7.47 (m, 15H, Ph-*H*); 1.11 (s, 9H, NCC*Me*$_3$)
11	7.63–7.33 (brm, 15H, Ph-*H*); 1.11 (s, 9H, NCC*Me*$_3$)
12 [b]	7.90–7.25 (brm, 20H, Ph-*H*, NCCH$_2$Ph-*H*); 3.81 (s, 2H, NCC*H*$_2$Ph)
13 [b]	7.55–7.28 (brm, 20H, Ph-*H*, NCCH$_2$Ph-*H*); 3.96 (s, 2H, NCC*H*$_2$Ph)
14 [b]	7.90–7.41 (brm, 20H, Ph-*H*, NCCH$_2$Ph-*H*); 3.82 (s, 2H, NCC*H*$_2$Ph)
15	7.67–7.42 (brm, Ph-*H*, NCPh-*H*)
16	7.48–7.31 (brm, Ph-*H*, NCPh-*H*)
17	7.62–7.41 (brm, Ph-*H*, NCPh-*H*)
18	7.77–7.48 (brm, Ph-*H*, NCPh-*H*)
19	7.41 (m, Ph-*H*, NCPh-*H*)
20	7.52–7.35 (brm, Ph-*H*, NCPh-*H*)
21	7.62–7.31 (brm, Ph-*H*)
22	7.52–7.40 (brm, Ph-*H*)
23	7.70–7.36 (brm, Ph-*H*)

[a] Spectra recorded in $CDCl_3$ (+25°C) referenced to $SiMe_4$ except [b] which were recorded in d^6 acetone (+25°C); brm = broad multiplet, m = multiplet, s = singlet, t = triplet, q = quartet.

Table 4
Low temperature ^{13}C NMR spectral data for selected seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes

Complex	^{13}C (δ) (ppm)
3 [b]	226.30 (s, $C{\equiv}O$); 218.76 (s, $C{\equiv}O$, $J_{w-c} = 64.38$ Hz); 200.18 (s, $C{\equiv}O$); 129.53–126.93 (m, Ph–C); 118.23 (s, $C{\equiv}N$); 24.58 (s, $C\text{H}_2\text{Ph}$)
6 [a]	238.55 (d, $J_{c-p} = 22$ Hz, $C{\equiv}O$); 212.42 (d, $J_{c-p} = 4.4$ Hz, $C{\equiv}O$); 209.56 (d, $J_{c-p} = 3.2$ Hz, $C{\equiv}O$); 135.92–127.13 (brm, Ph–C + $C{\equiv}N$); 12.03 (s, $C\text{H}_2\text{Me}$); 8.48 (s, CH_2Me)
7 [a]	237.21, 211.19, 208.98 (3s, $C{\equiv}O$); 135.93 (s, $C{\equiv}N$); 134.97–128.58 (brm, Ph–C); 12.01 (s, $\text{NC}C\text{H}_2\text{CH}_3$); 8.40 (s, NCCH_2CH_3)
8 [a]	208.98, 207.51, 205.87 (3s, $C{\equiv}O$); 132.51 (s, $C{\equiv}N$); 140.00–126.59 (m, Ph–C); 12.29 (s, $C\text{H}_2\text{Me}$) 8.39 (s, CH_2Me)
10 [b]	237.22, 210.81, 209.60 (3s, $C{\equiv}O$); 140.81 (s, $C{\equiv}N$); 134.51–126.27 (brm, Ph–C); 29.24 (s, $\text{NC}C\text{Me}_3$); 26.40 (s, $\text{NCC}Me_3$)
16 [a]	236.88, 211.08, 208.85 (3s, $C{\equiv}O$); 135.37–128.38 (brm, Ph–C, NCPh–C), 106.97 (s, $C{\equiv}N$).

[a] Recorded in CD_2Cl_2 (−65 °C) and referenced to $SiMe_4$.
[b] Recorded in $CDCl_3$ (−60 °C) and referenced to $SiMe_4$.
s = singlet, d = doublet, m = multiplet, brm = broad multiplet

$[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with two equivalents of NCR are likely to proceed via successive dissociative substitutions of acetonitrile with NCR because the complexes $[MI_2(CO)_3(NCMe)_2]$ obey the effective atomic number rule. It should be noted that Lucht et al. [20] have also reported the preparation of the bis(propionitrile) complex $[WI_2(CO)_3(NCEt)_2]$ from the reaction of *fac*-$[W(CO)_3(NCEt)_3]$ with one equivalent of I_2 in hexane.

The molecular structure of the bis(acetonitrile) complex $[WI_2(CO)_3(NCMe)_2]$, which was determined crystallographically [21], shows that the complex has the two iodo-ligands *trans* to each other, and also two *cis*-carbonyl and two *cis*-acetonitrile ligands, with a carbonyl ligand in the unique capping position of a capped octahedral geometry. The low temperature (−70°C, CD_2Cl_2) ^{13}C NMR spectrum for $[WI_2(CO)_3(NCMe)_2]$ [21] shows two carbonyl resonances at $\delta = 228.48$ and 202.36 in a 1 : 2 ratio. Colton and Kevekordes [22] have correlated the low temperature ^{13}C NMR carbonyl resonances with the solid-state structure of capped octahedral seven-coordinate carbonyl complexes. The low field resonance at 228.48 ppm for $[WI_2(CO)_3(NCMe)_2]$ [21] is assigned as the unique capping carbonyl group. In view of these observations, the low temperature ^{13}C NMR spectrum (−60°C, $CDCl_3$) of $[WI_2(CO)_3(NCCH_2Ph)_2]$ (**3**) showed three carbonyl resonances at $\delta = 226.30$, 218.76 and 200.18. Because there are three carbonyl resonances, the geometry could be distorted from the capped octahedral geometry of $[WI_2(CO)_3(NCMe)_2]$ [21], but it may be that the low field resonance at $\delta = 226.30$ is from a CO in a capped octahedral environment. It is likely that the greater steric requirements of the phenyl group compared with a hydrogen atom is responsible for the distortion from a capped octahedral geometry. Also, because the $NCCH_2Ph$ group can have several conformations of the phenyl group, it is possible that the observation of three ^{13}C NMR carbonyl resonances at −60°C for **3** reflects the conformations of the $NCCH_2Ph$ ligands rather than an inherently different coordination geometry around the tungsten centre. It should be noted that the room temperature (+25°C, $CDCl_3$) spectrum for **3** has one carbonyl resonance at $\delta = 218.28$, which indicates that the complex is undergoing a rapid fluxional process at room temperature.

The cyclic voltammograms for $[WI_2(CO)_3(NCR)_2]$ (R = Me, ^{t}Bu, CH_2Ph and Ph) in CH_2Cl_2 with scan rates of 50 mV s^{-1}, 100 mV s^{-1} and 200 mV s^{-1} all show irreversible one-electron oxidations at 1.02, 1.06, 1.01 and 1.01 V (with reference to a standard Calomel electrode) respectively. From these observations it appears that the R group does not significantly affect the electron-donating properties of the nitrile ligand in these complexes.

The reaction of $[MI_2(CO)_3(NCR)_2]$ (**1–5**) with an equimolar quantity of L (L = PPh_3, $AsPh_3$ or $SbPh_3$) in CH_2Cl_2 at room temperature gave the new mixed ligand complexes $[MI_2(CO)_3(NCR)L]$ (**6–20**). Complexes **6–20** were fully characterised by elemental analysis (C, H and N), (Table 1) and infrared (Table 2) and ^{1}H NMR spectroscopy (Table 3), and in selected cases by low temperature ^{13}C NMR spectroscopy (Table 4). Magnetic susceptibility measurements for complexes **2**, **4**, **7**, **8**, **13** and **16** showed the complexes to be diamagnetic, which was as expected because they also obey the effective atomic number rule. The complexes **6–20** are air-sensitive in solution, but are reasonably air-stable in the solid state. They are considerably more stable than the bis(nitrile) complexes **1–5**. Complexes **6–20** are soluble in chlorinated solvents, and partially soluble in diethyl ether and hydrocarbon media. They are less soluble than their bis(nitrile) counterparts. It should be noted that the phenylacetonitrile complexes $[MI_2(CO)_3(NCCH_2Ph)L]$ (**12–14**) are only sparingly soluble in chlorinated solvents, but are completely soluble in acetone. The IR spectra of **6–20** have three carbonyl bands in their IR spectra except in the case of complex **17**, which has four carbonyl bands (see Table 2). This indicates that there is one isomer in solution for complexes **6–16** and **18–20**.

The complexes $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**) and $[WI_2(CO)_3(NCPh)(AsPh_3)]$ (**16**) have been structurally characterised by X-ray crystallography. Crystals of **7** and **16** are composed of discrete monomeric molecules of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ and $[WI_2(CO)_3(NCPh)(AsPh_3)]$, respectively, held together by van der Waals' forces. In addition, compound **16** also contains molecules of Et_2O of crystallisation in the lattice (one

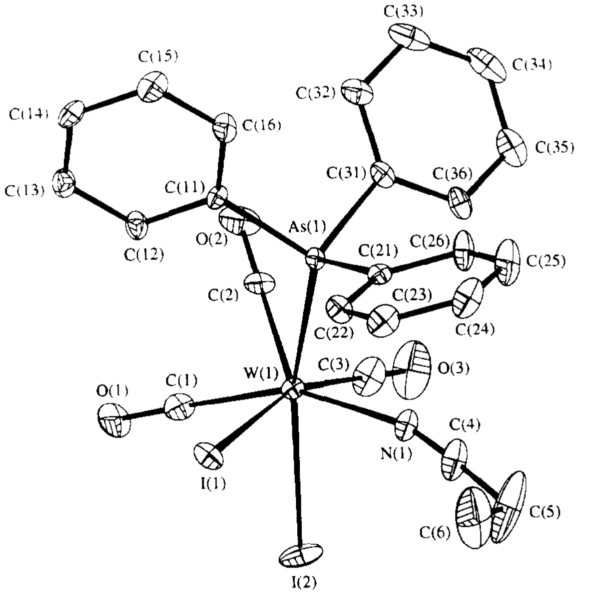

Fig. 1. X-ray crystal structure of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**).

molecule per molecule of complex); these are rather poorly defined because of partial disorder, but appear to have negligible interactions with the complex molecules.

The molecular structures of **7** and **16** are shown in Figs. 1 and 2, respectively, and the relevant bond lengths and angles are shown in Table 5. From the figures and data in Table 5, it is clear that the two molecules are similar in many respects. The tungsten atoms in both complexes have the same seven-coordinate, slightly distorted monocapped trigonal prismatic, coordination geometry with virtually identical ligand

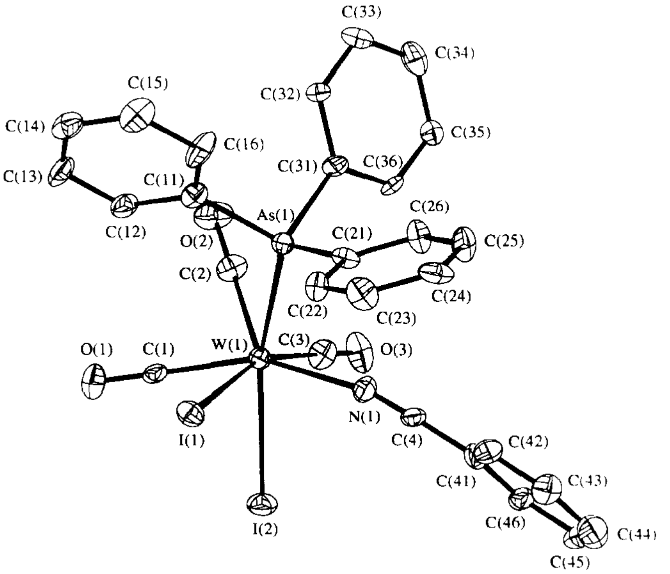

Fig. 2. X-ray crystal structure of $[WI_2(CO)_3(NCPh)(AsPh_3)]$ (**16**).

Table 5

Selected bond lengths [Å] and angles [deg] for $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**) and $[WI_2(CO)_3(NCPh)(AsPh_3)] \cdot Et_2O$ (**16**).

	(7)	**(16)**
W(1)–C(1)	1.997(7)	1.992(13)
W(1)–C(2)	1.975(6)	1.967(11)
W(1)–C(3)	1.992(7)	1.983(13)
W(1)–N(1)	2.168(5)	2.176(10)
W(1)–As(1)	2.6421(8)	2.633(2)
W(1)–I(1)	2.8629(6)	2.848(1)
W(1)–I(2)	2.8513(6)	2.833(1)
As(1)–C(11)	1.938(3)	1.946(6)
As(1)–C(21)	1.951(3)	1.938(5)
As(1)–C(31)	1.951(3)	1.957(5)
O(1)–C(1)	1.132(8)	1.16(2)
O(2)–C(2)	1.145(7)	1.15(1)
O(3)–C(3)	1.139(9)	1.15(2)
N(1)–C(4)	1.138(9)	1.118(14)
C(4)–C(5)	1.466(11)	
C(5)–C(6)	1.422(14)	
C(4)–C(41)		1.437(13)
C(2)–W(1)–C(1)	72.8(3)	72.8(5)
C(3)–W(1)–C(1)	105.3(3)	105.3(5)
C(2)–W(1)–C(3)	73.5(3)	72.0(5)
C(1)–W(1)–N(1)	154.2(2)	156.5(4)
C(2)–W(1)–N(1)	133.0(2)	130.5(5)
C(3)–W(1)–N(1)	85.4(3)	82.7(4)
C(1)–W(1)–As(1)	118.7(2)	117.1(4)
C(2)–W(1)–As(1)	70.6(2)	73.1(3)
C(3)–W(1)–As(1)	109.1(2)	112.0(4)
N(1)–W(1)–As(1)	77.83(14)	78.4(3)
C(1)–W(1)–I(1)	79.2(2)	79.5(3)
C(2)–W(1)–I(1)	124.0(2)	126.8(4)
C(3)–W(1)–I(1)	162.1(2)	160.6(4)
N(1)–W(1)–I(1)	83.95(14)	86.1(3)
As(1)–W(1)–I(1)	82.76(2)	80.88(4)
I(2)–W(1)–I(1)	88.24(2)	87.49(4)
C(1)–W(1)–I(2)	75.6(2)	76.5(3)
C(2)–W(1)–I(2)	127.9(2)	126.9(3)
C(3)–W(1)–I(2)	76.4(2)	75.7(4)
N(1)–W(1)–I(2)	84.58(14)	84.4(3)
As(1)–W(1)–I(2)	160.96(2)	159.72(4)
C(11)–As(1)–W(1)	117.79(11)	117.0(2)
C(21)–As(1)–W(1)	119.67(13)	118.7(2)
C(31)–As(1)–W(1)	107.69(12)	111.6(2)
C(11)–As(1)–C(21)	101.7(2)	103.2(3)
C(11)–As(1)–C(31)	106.0(2)	103.2(3)
C(31)–As(1)–C(21)	102.2(2)	100.9(3)
C(4)–N(1)–W(1)	164.4(6)	167.5(10)
O(1)–C(1)–W(1)	178.1(6)	178.7(12)
O(2)–C(2)–W(1)	179.6(6)	179.1(12)
O(3)–C(3)–W(1)	179.1(7)	178.7(11)
C(12)–C(11)–As(1)	119.8(2)	119.7(4)
C(16)–C(11)–As(1)	120.2(2)	120.3(4)
C(22)–C(21)–As(1)	118.8(2)	121.0(4)
C(26)–C(21)–As(1)	121.2(2)	119.0(4)
C(32)–C(31)–As(1)	123.6(2)	122.9(4)
C(36)–C(31)–As(1)	116.4(2)	117.1(4)
C(42)–C(41)–C(4)		118.8(7)
C(46)–C(41)–C(4)		121.2(7)
N(1)–C(4)–C(41)		176.8(13)
N(1)–C(4)–C(5)	174.3(9)	
C(6)–C(5)–C(4)	114.7(8)	

dispositions. Even the NCEt and NCPh groups in the two complexes are oriented in a similar way. The carbons of the three CO groups occupy the corners of one triangular face, the corners of the other triangular face being occupied by I(1), As(1) and N(1) atoms. The I(2) atom occupies the capping position on the rectangular face defined by C(1), C(3), N(1) and I(1) atoms.

The W–I and W–As distances in **7** [2.863, 2.851(1) Å; and 2.642(1) Å] are only marginally longer than the corresponding values in **16** [2.848, 2.833(1) Å; and 2.633(2) Å]. Although the two iodine atoms occupy different coordination sites in each compound, they are equidistant from the metal centre. The W–C(CO) distances in **7** [1.975–1.997(7) Å] are comparable with those in **16** [1.967–1.992(13) Å]; similarly, the W–N distances are also nearly the same [2.168(5) Å in **7** and 2.176(10) Å in **16**]. It is noteworthy in this context that the W–I, W–C(CO) and W–N(NCR) distances in the present complexes, which are seven-coordinate, are very close to the corresponding distances (within 0.02 Å) in several complexes of the type $[WI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$, [e.g. (R = ^{t}Bu, R′ = Me) [23]; (R,R′ = Me) [24], (R = Me, R′ = Ph) [24]; {R = $CH_2(3\text{-}C_4H_3S)$, R′ = Me} [25], which are all formally eight-coordinate; this suggests that there is very little, if any, influence of the coordination geometry on the metal–ligand bond lengths in these systems.

The C–O, N–C and C–C distances in the two complexes are as expected. The W–C–O groupings in both complexes are nearly linear (maximum deviation from linearity 1.9°), but deviations from linearity in the W–N–C–C moieties are much larger. Thus the W–N–C angles are 164.4(7)° (**7**) and 167.5 (10)° (**16**); the N–C–C angles are 174.3(9)° (**7**) and 176.8(13)° (**16**). These deviations are probably a result of the steric requirements of the Et and Ph groups in the two molecules. The requirements for minimum inter-ligand interactions are, presumably, also responsible for the $AsPh_3$ groups to adopt very similar orientations in the two complexes. Other bond angles in **7** are also very similar to the corresponding values in **16**, showing only small differences, up to a maximum of 4°.

Low temperature ^{13}C NMR spectroscopy was used to suggest solution state structures of several of the mixed ligand seven-coordinate complexes. The low temperature ^{13}C NMR spectra were obtained for complexes **7** and **16** and for the analogous $AsPh_3$-containing complex $[WI_2(CO)_3(NC^tBu)(AsPh_3)]$ (**10**), in order to ascertain whether the nitrile ligand affects the solution state geometry of the complexes. The low temperature (−65°C) ^{13}C NMR spectra of the crystallographically characterised complexes **7** and **16** were recorded in CD_2Cl_2 and showed three carbonyl bands at $\delta = 237.21$, 211.19, 208.98 and $\delta = 236.88$, 211.08, and 208.85, respectively. The three carbonyl resonances shown by complexes **7** and **16** conform with the solid-state structures shown in Figs 1 and 2. It should also be noted that the ^{13}C NMR (−60°C, $CDCl_3$) spectrum for $[WI_2(CO)_3(NC^tBu)(AsPh_3)]$ (**10**) has three carbonyl resonances $\delta = 237.22$, 210.81 and 209.60, and hence may have an analogous structure to **7** and **16**. In order to compare the propionitrile series $[WI_2(CO)_3(NCEt)L]$ (L = PPh_3, $AsPh_3$ and $SbPh_3$) (**6**–**8**) the low temperature (−65°C, CD_2Cl_2) ^{13}C NMR spectra of **6** and **8** were obtained. The spectrum for complex **6** shows resonances at $\delta =$ 238.55, 212.42 and 209.56 and complex **8** at $\delta = 208.98$, 207.51 and 205.87. Hence complex **6**, with L = PPh_3, and the crystallographically characterised complex **7** (L = $AsPh_3$) show very similar ^{13}C NMR carbonyl resonances, and are likely to have similar structures. In contrast the complex $[WI_2(CO)_3(NCEt)(SbPh_3)]$ (**8**) shows three carbonyl resonances with a very small spread of chemical shifts, the larger size and poorer σ-donating ability of $SbPh_3$ could be responsible for this, and may lead to distortion of the capped trigonal prismatic geometry to allow the three carbonyl ligands to be in similar environments.

The three complexes $[WI_2(CO)_3(PPh_3)(AsPh_3)]$ (**21**) and $[WI_2(CO)_3L_2]$ {L = $AsPh_3$ (**22**) and PPh_3 (**23**)} were prepared by treating $[WI_2(CO)_3(NCEt)_2]$ with one equivalent $AsPh_3$ in CH_2Cl_2 for 3 min to give $[WI_2(CO)_3(NCEt)(AsPh_3)]$, which when treated in situ with L = PPh_3 or $AsPh_3$ gave **21** and **22**, respectively. The bis(PPh_3) complex **23** was prepared by treating $[WI_2(CO)_3(NCEt)_2]$ with two equivalents of PPh_3 in CH_2Cl_2 at room temperature. Complexes **21** [11], **22** [26] and **23** [26], were reported previously and have been characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (Tables 1–3).

3. Experimental details

All reactions and purifications were carried out under dry nitrogen using standard vacuum/Schlenk line techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) were prepared by the published method [18]. All solvents were dried and purged with nitrogen before use. The chemicals used were obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (with helium as a carrier gas). Infrared spectra were recorded on a Perkin Elmer 1600 FT IR spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 CP MAS (^1H) at the University of Wales, Bangor, or on a Bruker WH 400 MHz (^{13}C) spectrometer at the University of Warwick. All ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane. Cyclic voltammetry measurements were recorded on an EG and G Princeton Applied Research Model 264A Polarographic Analyzer/Stripping Voltammeter connected to an EG and G Condecon 300 Controller. The measurements were controlled by microcomputer using the Condecon 310 cyclic voltammetry program. The cyclic voltammetry apparatus consisted of a 2 cm^3 electrochemical cell, a platinum counter electrode and a standard reference electrode. The solvent was dry degassed CH_2Cl_2 which contained 0.1 M of the electrolyte $[N^nBu_4][PF_6]$. Approximately 10–20 mg of the complex was used to produce a 10^{-3} mol dm^{-3} solution. Magnetic susceptibility measurements were determined using a Johnson-Matthey Magnetic Susceptibility balance.

3.1. Preparation of $[WI_2(CO)_3(NCEt)_2]$ (1)

To a stirred solution of $[WI_2(CO)_3(NCMe)_2]$ (1.3 g, 2.15 mmol) in CH_2Cl_2 (15 cm^3) under a stream of dry nitrogen was added an excess of NCEt (0.36 g, 0.46 cm^3, 6.46 mmol). After 20 h stirring, the solution was filtered. The solvent was removed in vacuo and the resulting brown product was washed with warm hexane (2 × 15 cm^3). Recrystallisation from CH_2Cl_2/Et_2O at −17°C produced analytically pure $[WI_2(CO)_3(NCEt)_2]$ (**1**) (Yield = 1.05 g, 77%).

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with an excess of NCR (where $R = {}^tBu$, Ph or CH_2Ph), and $[MoI_2(CO)_3(NCMe)_2]$ with an excess of NCPh, followed by subsequent recrystallisation from CH_2Cl_2/Et_2O at −17°C yielded the analogous complexes $[WI_2(CO)_3(NCR)_2]$ $R = {}^tBu$ (**2**), $R = CH_2Ph$(**3**) and R = Ph (**4**) and $[MoI_2(CO)_3(NCPh)_2]$ (**5**).

3.2. Preparation and characterisation of $[Mo(\mu\text{-}I)I(CO)_3(NC^tBu)]_2$

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.31 g, 0.60 mmol) in CH_2Cl_2 (15 cm^3) under dry nitrogen, was added an excess of NC^tBu (0.13 g, 0.17 cm^3, 2.4 mmol). After 30 min stirring the solution was filtered. The solvent was removed in vacuo and the resulting brown product was washed with warm hexane (2 × 15 cm^3) to afford the dimer $[Mo(\mu\text{-}I)I(CO)_3(NC^tBu)]_2$ (Yield = 0.3 g, 24%). Anal. Calc. for $C_{16}H_{18}N_2O_6I_4Mo_2$. C, 18.8; H, 1.8; N, 2.7. Found: C, 18.5; H, 2.5; N, 2.8%. IR ($CHCl_3$) $\nu(CO) = 2077$(m), 2011(s), 1960(s); $\nu(NC)$ 2258(w), 2236(w) cm^{-1} ^1H NMR ($CDCl_3$, 25°C) $\delta = 1.51$ (s, $NCCMe_3$).

3.3. Preparation of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (7)

To a stirred solution of $[WI_2(CO)_3(NCEt)_2]$ (0.2 g, 0.32 mmol) in CH_2Cl_2 (15 cm^3) under a stream of dry nitrogen was added $AsPh_3$ (0.097 g, 0.32 mmol). After 3 min stirring, the solution was filtered. The solvent was removed in vacuo to leave an orange powder, which was redissolved in the minimum amount of CH_2Cl_2. A few drops of diethyl ether were added and the solution was cooled to −17°C for 24 h to give orange single crystals of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**), suitable for X-ray crystallography. (Yield = 0.16 g, 56%).

Similar reactions of $[WI_2(CO)_3(NCR)_2]$ ($R = {}^tBu$, CH_2Ph and Ph) and $[MoI_2(CO)_3(NCPh)_2]$ with one equivalent of L (L = PPh_3, $AsPh_3$ and $SbPh_3$) followed by recrystallisation from CH_2Cl_2/Et_2O at −17°C gave the complexes $[WI_2(CO)_3(NCEt)(EPh_3)]$ {E = P(**6**)(1 min), Sb(**8**) (5 min)}, $[WI_2(CO)_3(NC^tBu)(EPh_3)]$ {E = P(**9**) (1 min), As(**10**) (3 min), Sb(**11**) (5 min)}, $[WI_2(CO)_3(NCCH_2Ph)(EPh_3)]$ {E = P(**12**) (1 min), As(**13**) (3 min), Sb(**14**) (5 min)} $[WI_2(CO)_3(NCPh)(EPh_3)]$ {E = P(**15**) (1 min), As(**16**) (3 min), Sb(**17**) (5 min)} and $[MoI_2(CO)_3(NCPh)(EPh_3)]$ {E = P(**18**) (1 min), As(**19**) (3 min), Sb(**20**) (5 min)}.

Recrystallisation of $[WI_2(CO)_3(NCPh)(AsPh_3)]$ (**16**) from CH_2Cl_2/Et_2O at −17°C for 24 h gave orange single crystals of $[WI_2(CO)_3(NCPh)(AsPh_3)]$ (**16**) suitable for X-ray crystallography.

Table 6
Crystal data and details of data collection and refinement for $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**) and $[WI_2(CO)_3(NCPh)(AsPh_3)] \cdot Et_2O$ (**16**)

	(**7**)	(**16**)
Formula	$C_{24}H_{20}NO_3I_2AsW$	$C_{28}H_{20}NO_3I_2AsW \cdot C_4H_{10}O$
M.W.	883.01	1005.14
Crystal system	Monoclinic	Orthorhombic
$a/Å$	11.465(3)	10.556(8)
$b/Å$	11.129(2)	16.332(5)
$c/Å$	20.950(2)	18.920(8)
$\alpha/°$	90	90
$\beta/°$	105.335(5)	90
$\gamma/°$	90	90
$V/Å^3$	2577.9(9)	3262(3)
Spac group	$P2_1/c$	$P2_12_12_1$
Z	4	4
$D_c/g\ cm^{-3}$	2.28	2.05
$F(000)$	1632	1896
μ (Mo–Kα)/cm^{-1}	82.4	64.8
Crystal size/mm^3	0.35 × 0.18 × 0.10	0.30 × 0.20 × 0.16
h_{min}, h_{max}	−15,12	−7,14
k_{min}, k_{max}	−14,11	−18,21
l_{min}, l_{max}	−27,24	−25,25
θ range/°	2.2–29.8	2.2–29.5
Total data measured	12834	10541
Total unique	6253	5405
R_{int}	0.0462	0.0493
Absorption correction factors, min, max	0.798, 1.125	0.862, 1.053
No. of parameters	254	298
$\rho_{min}, \rho_{max}/eÅ^{-3}$	−4.44,1.51	−1.15,1.67
$(\Delta/\sigma)_{max}$	0.001	0.011
R_1 [a]	0.0447(0.0366) [b]	0.0415(0.0334) [b]
wR_2 [a]	0.0999(0.0911) [b]	0.0977(0.0838) [b]

[a] $R_1 = \Sigma(\Delta F)/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(\Delta(F^2)^2)\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = 1/\sigma^2(F_o)^2$

[b] Values in the parentheses are calculated for data with $F_o^2 > 2\sigma(F_o^2)$.

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[WI_2(CO)_3(NCEt)(AsPh_3)]$.
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
W(1)	4673(1)	2378(1)	1303(1)	14(1)
I(1)	3457(1)	227(1)	1514(1)	22(1)
I(2)	6760(1)	1544(1)	2270(1)	35(1)
As(1)	2444(1)	3118(1)	750(1)	13(1)
O(1)	5865(4)	494(5)	562(3)	36(1)
O(2)	4540(4)	3461(5)	−88(3)	36(1)
O(3)	6423(6)	4590(6)	1530(4)	60(2)
N(1)	4109(5)	3039(5)	2148(3)	22(1)
C(1)	5419(5)	1181(6)	820(3)	24(1)
C(2)	4587(5)	3059(6)	421(3)	20(1)
C(3)	5782(7)	3788(7)	1452(4)	34(2)
C(4)	3851(6)	3121(7)	2635(4)	32(2)
C(5)	3480(10)	3101(12)	3253(5)	76(4)
C(6)	2568(12)	2244(9)	3269(5)	72(4)
C(11)	1520(3)	2266(3)	−26(2)	16(1)
C(12)	2021(3)	1274(3)	−258(2)	23(1)
C(13)	1356(3)	652(3)	−810(2)	25(1)
C(14)	190(3)	1021(4)	−1130(2)	23(1)
C(15)	−312(3)	2013(4)	−898(2)	28(1)
C(16)	353(3)	2635(3)	−346(2)	24(1)
C(21)	1284(3)	3221(3)	1282(2)	15(1)
C(22)	710(4)	2177(3)	1402(2)	20(1)
C(23)	−122(4)	2225(3)	1778(2)	28(1)
C(24)	−381(4)	3316(4)	2034(2)	32(2)
C(25)	193(4)	4359(3)	1913(2)	35(2)
C(26)	1025(4)	4311(3)	1537(2)	26(1)
C(31)	2536(4)	4781(2)	474(2)	18(1)
C(32)	2041(4)	5183(3)	−169(2)	24(1)
C(33)	2140(4)	6386(4)	−325(2)	35(2)
C(34)	2735(4)	7187(3)	162(2)	33(2)
C(35)	3230(4)	6785(3)	805(2)	29(2)
C(36)	3130(4)	5582(3)	961(2)	23(1)

3.4. Preparation of $[WI_2(CO)_3(AsPh_3)(PPh_3)]$ (21)

To a stirred solution of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (0.31 g, 0.35 mmol) in CH_2Cl_2 (15 cm^3) under a stream of dry nitrogen was added PPh_3 (0.09 g, 0.35 mmol). After 1 min of stirring the solution was filtered. The solvent was removed in vacuo to leave a yellow powder which was recrystallised from CH_2Cl_2/Et_2O at −17°C to give the analytically pure previously described complex $[WI_2(CO)_3(AsPh_3)(PPh_3)]$ (**21**) [11] (Yield = 0.14 g, 37%).

A similar reaction of $[WI_2(CO)_3(NCEt)(AsPh_3)]$ (**7**) with one equivalent of $AsPh_3$ and subsequent recrystallisation from CH_2Cl_2/Et_2O at −17°C gave the previously described complex $[WI_2(CO)_3(AsPh_3)_2]$ (**22**) [26].

3.5. Preparation of $[WI_2(CO)_3(PPh_3)_2]$ (23)

To a stirred solution of $[WI_2(CO)_3(NCEt)_2]$ (**1**) (0.25 g, 0.40 mmol) in CH_2Cl_2 (15 cm^3) under a stream of dry nitrogen were added two equivalents of PPh_3 (0.27 g, 0.79 mmol). After 10 min stirring the solution was filtered. The solvent was removed in vacuo to leave a yellow powder which was recrystallised from CH_2Cl_2/Et_2O to give the analytically pure previously described, complex $[WI_2(CO)_3(PPh_3)_2]$ (**23**) [26] (Yield = 0.16 g, 39%).

3.6. Crystal structure analysis of 7 and 16

All crystallographic measurements were made at 293 K using a Delft Insturments FAST TV area detector diffractometer positioned at the window of a rotating anode generator with Mo–Kα radiation (λ = 0.71069

Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[WI_2(CO)_3(NCPh)(AsPh_3)] \cdot Et_2O$.
U_{eq} is defind as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
W(1)	517(1)	746(1)	−145(1)	21(1)
As(1)	−1514(1)	−183(1)	−237(1)	22(1)
I(1)	973(1)	−308(1)	1028(1)	31(1)
I(2)	2345(1)	1822(1)	439(1)	34(1)
O(1)	3108(10)	−59(6)	−593(5)	46(3)
O(2)	262(9)	222(7)	−1723(4)	44(3)
O(3)	258(8)	2350(6)	−1041(5)	42(3)
N(1)	−798(10)	1389(6)	545(5)	28(2)
C(1)	2160(12)	246(8)	−432(6)	26(3)
C(2)	353(12)	422(8)	−1142(6)	29(3)
C(3)	360(13)	1757(8)	−718(6)	30(3)
C(4)	−1287(11)	1738(8)	974(6)	26(3)
C(11)	−1244(8)	−1348(4)	−392(4)	33(3)
C(12)	−77(7)	−1624(5)	−635(4)	32(3)
C(13)	121(7)	−2455(5)	−746(4)	38(4)
C(14)	−848(9)	−3011(4)	−614(4)	37(3)
C(15)	−2015(8)	−2736(4)	−371(4)	44(4)
C(16)	−2213(6)	−1904(5)	−260(4)	42(4)
C(21)	−2734(6)	−160(5)	528(3)	19(2)
C(22)	−2568(6)	−641(5)	1127(4)	30(3)
C(23)	−3475(8)	−634(5)	1660(3)	37(3)
C(24)	−4547(6)	−146(6)	1594(3)	38(4)
C(25)	−4712(6)	335(5)	995(4)	35(3)
C(26)	−3806(7)	329(5)	462(3)	30(3)
C(31)	−2584(7)	136(4)	−1036(3)	27(3)
C(32)	−3193(8)	−430(4)	−1467(4)	34(3)
C(33)	−3948(8)	−162(5)	−2023(4)	45(4)
C(34)	−4093(7)	672(6)	−2148(4)	38(3)
C(35)	−3483(8)	1237(4)	−1717(4)	33(3)
C(36)	−2729(8)	969(4)	−1161(4)	26(3)
C(41)	−1866(8)	2223(5)	1519(4)	30(3)
C(42)	−2600(8)	1833(4)	2028(4)	35(3)
C(43)	−3144(8)	2284(6)	2572(4)	37(3)
C(44)	−2954(9)	3125(6)	2607(4)	56(5)
C(45)	−2221(9)	3515(4)	2098(4)	42(4)
C(46)	−1677(8)	3064(5)	1554(4)	29(3)
C(01) [a]	−6488(15)	1791(10)	2518(8)	45(4)
C(02) [a]	−7111(24)	1079(19)	2875(25)	362(36)
C(03) [a]	−8881(17)	2077(12)	3155(9)	66(5)
C(04) [a]	−9950(18)	2489(14)	3522(11)	86(7)
O(01) [a]	−8186(23)	1571(15)	2662(12)	197(11)

[a] Atoms in the Et_2O solvent, refined with isotropic temperature factors.

Å) by following procedures described in Ref. [27]. The crystal data and details of data collection and structure refinement are presented in Table 6.

The structures were solved by direct methods using the program SHELX-86 [28] and refined by full-matrix least-squares, initially using the program SHELX-80 [29]. Although the overall structures appeared to be correct, giving conventional R-values of ca. 0.06 in both cases, three phenyl carbons in the **16** gave "unreasonable" anisotropic displacement coefficients. This, combined with the fact that the mosaicity of this crystal was also very high [2.11° cf. 0.98° for **7**], suggested that there was some kind of disorder or other unrecognised effect. The structures were then re-examined and refinement continued with the help of the program SHELXL-93 [30], using all unique F_0^2 data. Refinement of **7** proceeded smoothly, but the structure of **16** was indicated to be a possible racemic twin [Flack's absolute structure parameter ca. 0.17] [31]. This was dealt with by applying a racemic twin matrix TWIN -1 0 0 0 -1 0 0 0 -1 2 and refining the BASF scale factor which had a final value of 0.173(12). The previously "unreasonable" phenyl carbons now gave acceptable displacement coefficients and the refinement converged without any difficulty. The structure of **16** was also found to contain one disordered molecule of Et_2O per molecule of complex; the Et_2O was refined isotropically with bond length restraints C–C 1.500(5) Å and C–O 1.450(5) Å. The final wR_2 values based on all unique F^2 are 0.0999 (compound **7**) and 0.0977 (compound **16**); the corresponding conventional R values are 0.0447 and 0.0415 for all data. In both cases, the phenyl rings were treated as idealised hexagons (C–C = 1.390 Å). The hydrogens on Et_2O in **16** were ignored; all others were included in idealised positions with U_{iso}'s set at 1.2 times the U_{eq}'s of the parent carbons. Both data sets were corrected for absorption using the program DIFABS [32]. The successful refinement of **16**, along with others, is an excellent example in which SHELXL-93 has proved to be very effective in dealing with disordered/twinned structures. Sources of scattering factors are as in Ref. [30]. The calculations were done on a 486DX2/66 personal computer. Selected bond lengths and angles and atomic coordinates are given in Tables 5, 7 and 8. Tables of anisotropic displacement parameters of the non-hydrogen atoms, hydrogen atom parameters and complete lists of bond lengths and angles for complexes **7** and **16** have been deposited at the Cambridge Crystallographic Data Centre.

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