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Isocyanide derivatives of tungstenocene

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Abstract

The synthesis and reactions of the tungstenocene isocyanide complexes [Cp₂WCNR] (**2a**: R = Et; **2b**: R = ^tBu; **2c**: R = Me) with electrophiles are reported. Complexes **2a** and **2b** are obtained from Cp₂WCl₂ in two steps. The first involves chloride abstraction from Cp₂WCl₂ by TlPF₆ in the presence of RNC and affords the W^{IV} isocyanide complexes [Cp₂WCl(CNR)]PF₆ (**1a**: R = Et; **1b**: R = ^tBu). The second step is the reductive dehalogenation of **1a** and **1b** by sodium amalgam to give **2a** and **2b** in high yields. The electron-rich tungstenocene complexes **2a–2c** undergo electrophilic addition exclusively at the metal centre. Thus, treatment of **2a** with Et₃OBF₄ affords the W^{IV} ethyl complex [Cp₂WEt(CNEt)]BF₄ (**3a**). Similarly alkylation of **2b** and **2c** with MeI gives the methyl complexes [Cp₂WMe(CNR)]I (**4b**: R = ^tBu; **4c**: R = Me). The crystal structure of **1a** reveals a pseudotetrahedral coordination geometry around the tungsten center with the Cp ligands adopting an eclipsed conformation. The structural parameters of **1a** exhibit values close to those for other Cp₂W^{IV} derivatives, with the ethylisocyanide ligand adopting a linear coordination mode.

1. Introduction

Following our studies on the activation of isocyanides and nitriles by transition metals [1] we recently reported the synthesis and reactivity of isocyanide derivatives of group VI metallocenes [2]. The complexes described fall into two main categories: (i) the cationic M^{IV} derivatives such as [Cp₂Mo(CNMe)₂]²⁺ and [Cp₂MX(CNR)]⁺ (R = Me, Et, ^tBu; X = Cl, Br, I, H, Me, Et) and (ii) the neutral M^{II} derivatives such as [Cp₂Mo(CNR)] (R = Me, Et, ^tBu). These studies revealed that the electron rich molybdenocene complexes [Cp₂Mo(CNR)] undergo electrophilic addition of both organic and inorganic electrophiles exclusively at the metal centre to yield cationic Mo^{IV} isocyanide complexes of the general formula [Cp₂Mo(E)(CNR)]⁺ (E = electrophile) [2b]. The alkyl derivatives [Cp₂MoR'(CNR)]⁺ rearrange, when heated in CH₂Cl₂, to the η²-iminoacyl complexes [Cp₂Mo(η²-R'C=NR)]⁺ [2b]. In contrast, the complex [Cp₂Mo(CNMe)₂]²⁺ undergoes nucleophilic addition of amines, alkoxides and thiolates at the isocyanide ligand

to give carbene complexes or hydride addition at one of the Cp rings to give the cyclopentadiene complex [CpMo(η⁴-C₅H₆)(CNMe)₂]⁺ [2c].

One of the most striking results of the above work was the observation of the unusual nature of the M–CNR bond in the Cp₂M^{II} derivatives, as exemplified by the spectroscopic and the X-ray diffraction data for the electron-rich molybdenocene complex [Cp₂Mo(CN-^tBu)] *viz.*: (ν(C≡N^tBu) in THF 1845 cm⁻¹; isocyanide carbon resonance in C₆D₆ δ 241.0 ppm; extensive bending of the isocyanide ligand at nitrogen angle C–N–C 139.5(4)° [2b]. These properties indicate a very strong back-donation from the Cp₂Mo fragment to the isocyanide ligand, a feature that has been found important for the activation of isocyanide ligands towards electrophilic attack at the nitrogen atom [3]. In continuation of this work on electron-rich isocyanide complexes we describe below a convenient synthesis of the tungstenocene complexes [Cp₂W(CNR)] and report on their reactions with electrophiles.

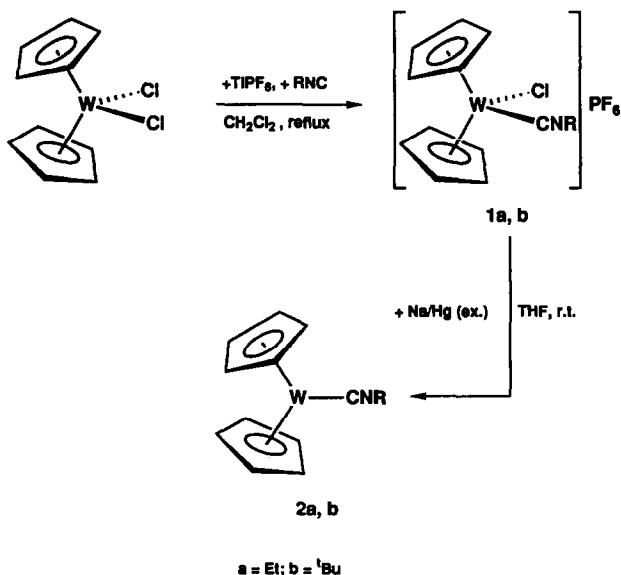
2. Results and discussion

It was recently reported that reductive dehalogenation of Cp₂MCl₂ by Na/Hg in the presence of RNC is

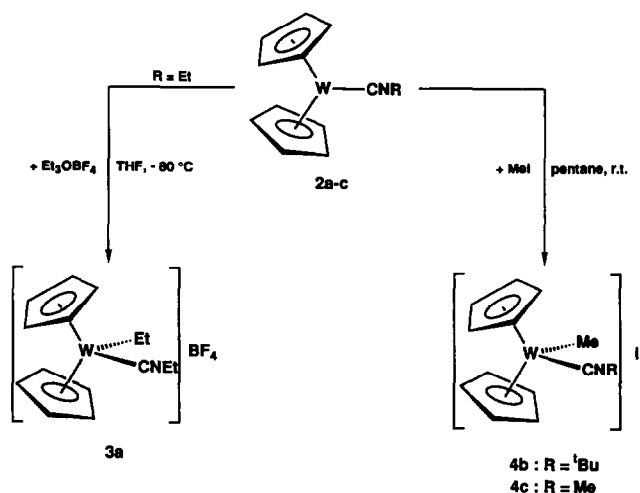
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one of the possible ways of preparing the metallocene isocyanide complexes $[\text{Cp}_2\text{M}(\text{CNR})]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{Me}$) [2a, 2c]. However this route has two major disadvantages, namely (i) the yields are irreproducible and low, being 40% in the most favourable case, and (ii) a large excess of RNC is needed for the synthesis of $[\text{Cp}_2\text{M}(\text{CNR})]$. Later two considerably improved synthetic methods were developed for the molybdenocene derivatives $[\text{Cp}_2\text{Mo}(\text{CNR})]$ ($\text{R} = \text{Et}, ^t\text{Bu}$) involving substitution of the labile acetonitrile ligand in $[\text{Cp}_2\text{Mo}(\eta^2\text{-MeCN})]$ by RNC or reductive dehalogenation of the Mo^{IV} isocyanide complexes $[\text{Cp}_2\text{MoX}(\text{CNR})]\text{PF}_6$ ($\text{X} = \text{Cl}, \text{I}$) by Na/Hg [2b,4]. However the lack of any readily available Cp_2WL complexes ($\text{L} = \text{CO}, \text{alkene}, \text{alkyne}, \text{nitrile}$) [5], for example, the acetonitrile derivative $[\text{Cp}_2\text{W}(\eta^2\text{-MeCN})]$ was made by an elaborate procedure involving reductive elimination of methane from $[\text{Cp}_2\text{W}(\text{H})\text{Me}]$ in the presence of MeCN [5d,6], precluded the application of the first method to the preparation of the desired W^{II} complexes $[\text{Cp}_2\text{W}(\text{CNR})]$. We therefore decided to examine reductive dehalogenation of the W^{IV} isocyanide complexes $[\text{Cp}_2\text{WX}(\text{CNR})]\text{PF}_6$ as possibly the best approach and Scheme 1 depicts the results obtained.

The preparation of the required ionic complexes was readily achieved by treatment of the parent Cp_2WCl_2 with TIPF_6 and a slight excess of the isocyanide in refluxing CH_2Cl_2 . The complexes $[\text{Cp}_2\text{WCl}(\text{CNR})]\text{PF}_6$ (**1a**: $\text{R} = \text{Et}$; **1b**: $\text{R} = ^t\text{Bu}$) were obtained as thermally stable, orange-red crystalline solids, soluble in MeCN and CH_2Cl_2 , but sparingly soluble in THF.



Scheme 1. Synthesis of the tungstenocene isocyanide complexes $[\text{Cp}_2\text{W}(\text{CNR})]$.



Scheme 2. Reactions of the tungstenocene isocyanide complexes $[\text{Cp}_2\text{W}(\text{CNR})]$ with electrophiles.

Reduction of **1a** and **1b** with an excess of sodium amalgam in THF afforded the tungstenocene isocyanide complexes $[\text{Cp}_2\text{W}(\text{CNR})]$ (**2a**: $\text{R} = \text{Et}$; **2b**: $\text{R} = ^t\text{Bu}$) in high yield (Scheme 1). These were isolated as very air sensitive brown, microcrystalline solids, soluble in all common organic solvents.

The tungstenocene derivatives **2a** and **2b** were found, like other Cp_2ML complexes, to react readily with electrophiles [7]. Addition of the electrophile occurs exclusively at the metal centre. Thus treatment of **2a** with Et_3OBF_4 afforded the W^{IV} ethyl complex $[\text{Cp}_2\text{WEt}(\text{CNEt})]\text{BF}_4$ (**3a**) in quantitative yield (Scheme 2). Complex **3a** was isolated as a yellow, microcrystalline solid, soluble in MeCN and CH_2Cl_2 . Similarly reaction of **2b** or the analogous methylisocyanide derivative $[\text{Cp}_2\text{W}(\text{CNMe})]$ (**2c**) with MeI was accompanied by a fast colour change from brown to yellow and quantitative precipitation of the W^{IV} methyl complexes $[\text{Cp}_2\text{WMe}(\text{CNR})]\text{I}$ (**4b**: $\text{R} = ^t\text{Bu}$; **4c**: $\text{R} = \text{Me}$) (Scheme 2). No evidence for electrophile addition at the isocyanide nitrogen was obtained in these reactions, in agreement with the results of an Extended Hückel molecular orbital calculation on $[\text{Cp}_2\text{Mo}(\text{CNMe})]$, which showed that the HOMO of this complex is mainly localized on the metal and has a much higher energy than the orbital assigned to the isocyanide nitrogen lone pair [2b].

Complex **3a** was found to be considerably more stable than the molybdenum analogue $[\text{Cp}_2\text{MoEt}(\text{CNEt})]\text{BF}_4$, remaining unchanged even after prolonged refluxing of its solution in acetonitrile. This contrasts with the relatively easy migration of the metal bound ethyl group to the adjacent isocyanide ligand in $[\text{Cp}_2\text{MoEt}(\eta^2\text{-EtC}=\text{NEt})]\text{BF}_4$ [2b]. This difference in re-

activity can be accounted for in terms of the lower energy barrier generally observed for alkyl migrations in molybdenum isocyanide complexes than for their tungsten analogues [1b,1c,8].

3. Spectroscopic investigations

3.1. IR spectra

The IR spectra of all the compounds are in agreement with the proposed structures and are summarized in Table 1.

The $\nu(\text{C}\equiv\text{NR})$ absorptions of the W^{IV} halo-isocyanide complexes **1a** and **1b** appear at higher wavenumbers (*ca.* 40 cm^{-1}) than those of the free isocyanides. This reveals a bonding situation in which an essentially σ donation from the isocyanide ligand to the $[\text{Cp}_2\text{WCl}]^+$ fragment is present, and this is confirmed by the crystal structure of **1a** discussed below. This shift to higher wavenumbers is less pronounced in the W^{IV} alkyl complexes **3a**, **4b** and **4c**, in which the alkyl substituent renders the metal centre more electron-rich. In contrast, the $\nu(\text{C}\equiv\text{NR})$ absorptions of the W^{II} complexes $[\text{Cp}_2\text{W}(\text{CNR})]$ (**2a**, **2b**) show a pro-

TABLE 1. $\nu(\text{C}\equiv\text{NR})$ absorptions for the complexes **1a–4c** in cm^{-1}

Complex	$\nu(\text{C}\equiv\text{NR})$	Solvent
$[\text{Cp}_2\text{WCl}(\text{CNEt})]\text{PF}_6$ (1a)	2207 s, 2192s, br	CH_2Cl_2
$[\text{Cp}_2\text{WCl}(\text{CN}^t\text{Bu})]\text{PF}_6$ (1b)	2178 s	CH_2Cl_2
$[\text{Cp}_2\text{W}(\text{CNEt})]$ (2a)	1873 w, 1810 s	THF
$[\text{Cp}_2\text{W}(\text{CN}^t\text{Bu})]$ (2b)	1822 s	THF
$[\text{Cp}_2\text{WEt}(\text{CNEt})]\text{BF}_4$ (3a)	2164 s	CH_2Cl_2
$[\text{Cp}_2\text{WMe}(\text{CN}^t\text{Bu})]\text{I}$ (4b)	2139 s	CH_2Cl_2
$[\text{Cp}_2\text{WMe}(\text{CNMe})]\text{I}$ (4c)	2170 s	KBr

nounced opposite shift, appearing at considerably lower frequencies than those for the free isocyanides ($\nu(\text{C}\equiv\text{NEt})$ in THF: 2149 cm^{-1} ; $\nu(\text{C}\equiv\text{N}^t\text{Bu})$ in THF: 2140 cm^{-1}), and even slightly lower than those for their molybdenum analogues (*e.g.* **2b**: $\nu(\text{C}\equiv\text{N}^t\text{Bu})$ in THF = 1822 cm^{-1} ; $[\text{Cp}_2\text{Mo}(\text{CN}^t\text{Bu})]$: $\nu(\text{C}\equiv\text{N}^t\text{Bu})$ in THF = 1845 cm^{-1}) [2b]. In fact comparably low

TABLE 2. ^1H NMR data for the complexes **1a–4c** at 20°C; relative intensities and multiplicities in parentheses, coupling constants in Hz

Complex	WCH_3 WCH_2CH_3	CNCH_2CH_3	$\text{CNC}(\text{CH}_3)_3$	CNCH_3 CNCH_2CH_3	Cp	Solvent
1a	–	1.42 (3, t) $^3J(\text{H,H})$ 7.3	–	4.15 (2, q) $^3J(\text{H,H})$ 7.3	5.69 (10, s)	CD_3CN
1b	–	–	1.57 (9, s)	–	5.68 (10, s)	CD_3CN
2a	–	1.03 (3, t) $^3J(\text{H,H})$ 7.3	–	3.21 (2, q) $^3J(\text{H,H})$ 7.3	4.28 (10, s)	C_6D_6
2b	–	–	1.15 (9, s)	–	4.27 (10, s)	C_6D_6
3a	0.96 (2, q) $^3J(\text{H,H})$ 7.3; 1.27 (3, t) $^3J(\text{H,H})$ 7.3	1.36 (3, t) $^3J(\text{H,H})$ 7.3	–	3.92 (2, q) $^3J(\text{H,H})$ 7.3	5.20 (10, s)	CD_3CN
4b	0.13 (3, s) $^2J(\text{W,H})$ 6.1	–	1.54 (9, s)	–	5.36 (10, s)	CD_2Cl_2
4c	0.09 (3, s)	–	–	3.70 (3, s)	5.21 (10, s)	CD_3CN

TABLE 3. ^{13}C (^1H) NMR data for the complexes **1a–4c** at 20°C; coupling constants in Hz

Complex	WCH_3 WCH_2CH_3	CNCH_2CH_3	WCH_2CH_3	CMe_3	CNCH_3 CNCH_2CH_3	CMe_3	Cp	CNR	Solvent
1a	–	15.4	–	–	42.3	–	95.4	– ^a	CD_3CN
1b	–	–	–	30.5	–	61.7	95.6	130.2	CD_3CN
2a	–	15.8	–	–	40.9	–	72.3	244.0	C_6D_6
2b	–	–	–	30.6	–	52.8	72.1	237.4	C_6D_6
3a	–19.1 $^1J(\text{W,C})$ 54.9	15.7	22.9	–	42.0	–	89.7	144.6	CD_3CN
4b	–33.5 $^1J(\text{W,C})$ 58.5	–	–	31.0	–	60.6	89.9	149.7	CD_2Cl_2
4c	–34.5	–	–	–	32.3	–	90.0	143.7	CD_3CN

^a The isocyanide carbon resonance could not be observed due to the low solubility of the complex **1a** in CD_3CN .

$\nu(\text{C}\equiv\text{NR})$ frequencies were previously observed only for electron-rich W^0 isocyanide complexes such as $\text{W}(\text{CNet})_6$ ($\nu(\text{C}\equiv\text{NEt})$ in THF = 1987, 1868 cm^{-1}) [1a], $\text{Na}[\text{Cp}^*\text{W}(\text{CO})_2(\text{CNet})]$ ($\nu(\text{C}\equiv\text{NEt})$ in THF = 1855 cm^{-1}) [1b], *trans*- $\text{W}(\text{CN}^t\text{Bu})_2(\text{dppe})_2$ ($\nu(\text{C}\equiv\text{N}^t\text{Bu})$ in THF = 1904 cm^{-1}) [9]. These results indicate extensive back-donation from the $\text{Cp}_2\text{W}^{\text{II}}$ fragment to the isocyanide ligand in **2a** and **2b** in keeping with the results obtained previously for the molybdenum analogues [$\text{Cp}_2\text{Mo}(\text{CNR})$] [2b].

3.2. NMR spectra

Further support for the assigned structures to **1a–4c** was provided by the ^1H NMR spectra, which all display a characteristic singlet resonance from the two equivalent Cp ligands (Table 2).

This resonance is shifted downfield on going from the W^{II} complexes **2a** and **2b** to the W^{IV} compounds **1a**, **1b**, **3a**, **4b** and **4c**. Furthermore the chemical shifts of the Cp protons are in good agreement with those found for the corresponding molybdenum complexes [2b].

The most interesting feature of the ^{13}C NMR spectra is the extremely low-field resonance observed for the isocyanide-carbon of the tungstenocene derivatives **2a** and **2b** (δ 244.0 and 237.4, respectively) (Table 3). In fact these chemical shifts are the highest so far reported for electron-rich tungsten isocyanide complexes (e.g. $\text{W}(\text{CNet})_6$; δ 178.6 [1a]; $\text{Cp}^*(^t\text{BuNC})_2\text{W}\equiv\text{CNet}_2$; δ 221.8 [1e]; $\text{Tp}'(\text{EtNC})_2\text{W}\equiv\text{CNet}_2$; δ 222.6 [10]) and in agreement with the IR data, reflect the unusual ability of the $\text{Cp}_2\text{W}^{\text{II}}$ fragment to engage in back-donation with the RNC ligand [11].

3.3. Crystal structure of [$\text{Cp}_2\text{WCl}(\text{CNet})$] PF_6 (**1a**)

The molecular structure of **1a** was confirmed by a single-crystal X-ray diffraction study. Two views of the cation of **1a** with the atom numbering scheme are given in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 4, and atomic coordinates in Table 5.

The crystal consists of discrete [$\text{Cp}_2\text{WCl}(\text{CNet})$] cations and PF_6 anions. The coordination geometry of the cation can be described as distorted tetrahedral if it is assumed that the Cp ligands occupy single coordination sites. The cation has approximately C_s symmetry, the symmetry plane being defined by the atoms W, C(1) and Cl (Fig. 1).

The structural parameters around the tungsten centre exhibit values similar to those observed for other [Cp_2MXL] $^+$ complexes (M = Mo, W; X = 1e donor ligand; L = 2e donor ligand) [12]. Thus the C(1)–W–Cl angle of 81.3(3) $^\circ$ is not significantly different from the X–M–L angle observed in [$\text{Cp}_2\text{WBr}(\text{CNMe})$] $^+$ [(Br–W–C) $_{\text{av.}}$ = 82.7 $^\circ$] [2c]. Also the angle between the ring

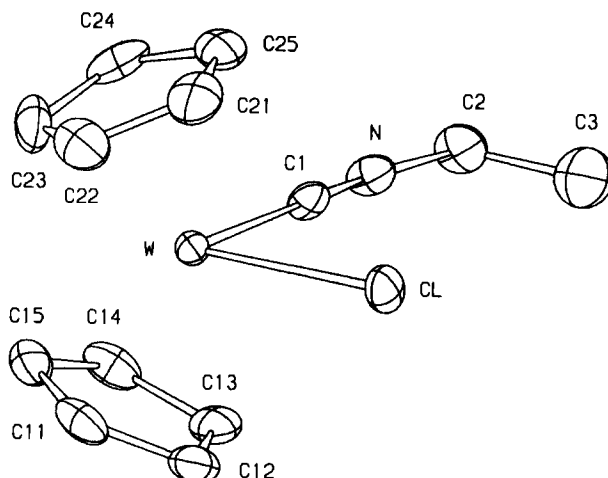


Fig. 1. ORTEP plot of the cation in **1a** with thermal ellipsoids drawn at the 20% level.

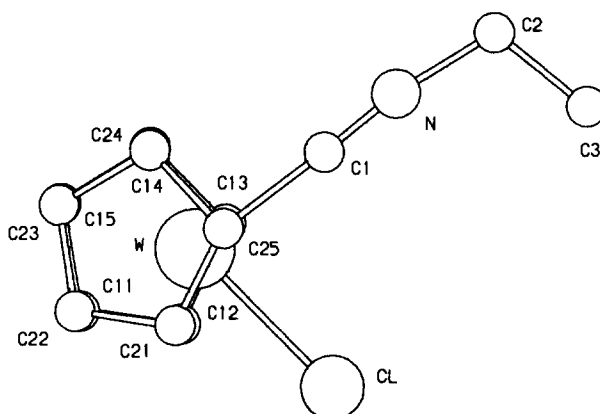


Fig. 2. Projection of the cation in **1a** on to the C(1)–W–Cl plane.

TABLE 4. Selected bond lengths (pm) and bond angles (grad) with estimated standard deviations for **1a**^a

W–C(1)	203.6(10)	W–Cl	245.9(3)
W–C(11)	232.0(13)	C(1)–N	116.2(13)
W–C(12)	237.9(13)	N–C(2)	144.2(16)
W–C(13)	226.3(12)	C(1)–W–Cl	81.3(3)
W–C(14)	225.8(13)	C(1)–W–cp ₁	105.0
W–C(15)	226.7(13)	C(1)–W–cp ₂	106.5
W–C(21)	233.9(16)	Cl–W–cp ₁	106.3
W–C(22)	234.3(16)	Cl–W–cp ₂	106.6
W–C(23)	227.5(17)	cp ₁ –W–cp ₂	137.0
W–C(24)	224.2(15)	W–C(1)–N	177.3(9)
W–C(25)	224.7(13)	C(1)–N–C(2)	172.7(11)
W–cp ₁	197.2	N–C(2)–C(3)	110.1(12)
W–cp ₂	196.6		

^a cp₁ and cp₂ refer to the computed centroids of the cyclopentadienyl rings.

TABLE 5. Atomic parameters for **1a**

Atom	x	y	z	U_{eq}
W	0.16649(2)	0.16838(3)	0.30714(3)	0.035(1)
Cl	0.2770(2)	0.3392(3)	0.2950(3)	0.062(2)
C(1)	0.2025(6)	0.1051(10)	0.1559(8)	0.047(4)
N	0.2224(6)	0.0641(10)	0.0709(8)	0.059(4)
C(2)	0.2562(9)	0.0254(14)	-0.0316(10)	0.074(5)
C(3)	0.3297(12)	0.1160(19)	-0.0459(16)	0.111(6)
C(11)	0.2128(10)	0.1175(13)	0.5154(10)	0.074(5)
C(12)	0.2946(9)	0.1276(12)	0.4821(11)	0.069(5)
C(13)	0.2890(8)	0.0383(13)	0.3902(11)	0.069(5)
C(14)	0.2064(10)	-0.0338(10)	0.3729(12)	0.075(5)
C(15)	0.1594(9)	0.0185(13)	0.4500(11)	0.073(5)
C(21)	0.0696(10)	0.3477(14)	0.2535(16)	0.088(6)
C(22)	0.0417(10)	0.2834(16)	0.3424(14)	0.087(6)
C(23)	0.0132(9)	0.1631(16)	0.3005(17)	0.101(6)
C(24)	0.0219(8)	0.1513(15)	0.1814(15)	0.087(6)
C(25)	0.0601(8)	0.2682(14)	0.1551(12)	0.073(5)
P	0.0415(2)	0.2740(3)	0.7460(3)	0.051(1)
F(1)	0.1467(5)	0.2759(11)	0.7517(11)	0.119(5)
F(2)	0.0234(10)	0.1709(11)	0.6434(12)	0.166(6)
F(3)	-0.0643(5)	0.2741(11)	0.7360(9)	0.116(5)
F(4)	0.0550(9)	0.3800(12)	0.8443(11)	0.159(6)
F(5)	0.0238(7)	0.3794(11)	0.6419(10)	0.128(5)
F(6)	0.0553(9)	0.1727(10)	0.8483(10)	0.141(6)

normals of 136.8° is close to that observed in other Cp_2W^{IV} derivatives [13]. The cyclopentadienyl ligands are pentahapto coordinated, and adopt an eclipsed conformation (Fig. 2). The W–C_{Cp} distances range for the one Cp ring from 225.8(13) to 237.9(13) pm, with a mean value of 229.8 pm and for the other Cp ring from 224.2(15) to 234.4(16) pm, with a mean value of 229.0 pm. These values are similar to those reported for other bis(cyclopentadienyl)tungsten(IV) complexes [13]. Also the W–Cl bond length of 245.7(3) pm lies in the normal range for other W^{IV} chloro complexes [14].

The ethyl isocyanide ligand adopts a linear coordination mode as indicated by the angle at the nitrogen atom [C(1)–N–C(2) = $172.7(12)^\circ$] (Table 4). The C(1)–N distance of 116.2(13) pm corresponds to that of a carbon nitrogen triple bond [15].

4. Experimental details

Standard Schlenk procedures were used for all preparations and sample manipulations. The solvents were dried by standard methods (n-pentane, Et₂O and THF over Na/benzophenone; CH₂Cl₂ over P₂O₅ and Na/Pb alloy) and distilled under nitrogen prior to use or stored over 4 Å molecular sieves.

Elemental analyses were performed by the Microanalytical Laboratory of the Anorganisch-chemisches Institut der TU München. IR spectra were recorded on a Nicolet DX 5 FT spectrophotometer. ¹H and ¹³C{H} NMR spectra were recorded in dried, deoxygenated,

deuterated solvents on a Jeol GX 400 FT instrument. Chemical shifts were referenced to residual solvent signals (CD₃CN δ_H 1.93 and δ_C 118.2 ppm; C₆D₆ δ_H 7.15 and δ_C 128.0 ppm; CD₂Cl₂ δ_H 5.32 and δ_C 53.8 ppm). Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer; *m/z* values relate to the ¹⁸⁴W and ³⁵Cl isotopes.

The complexes Cp₂WCl₂ and [Cp₂W(CNMe)] were prepared as described in refs. 16 and 2c, respectively. EtNC and ^tBuNC were made by published procedures [17,18], distilled, and stored under nitrogen. Et₃OBf₄ was obtained by Meerwein's method [19].

4.1. [Cp₂WCl(CNEt)]PF₆ (**1a**)

To a suspension of Cp₂WCl₂ (720 mg, 1.87 mmol) in 50 ml of CH₂Cl₂ was added CNEt (0.15 ml, 2.02 mmol) and TlPF₆ (700 mg, 2.00 mmol). The mixture was refluxed for 12 h until all the green solid had dissolved. After cooling to room temperature the white precipitate of TlCl was allowed to settle and the supernatant orange solution filtered. The filtrate was reduced in volume and Et₂O slowly added until precipitation was complete. The precipitate was recrystallized from CH₂Cl₂/Et₂O to give orange-red crystals of **1a**. Yield: 950 mg (92%). Found: C, 28.48; H, 2.79; Cl, 6.24; N, 2.55; W, 32.88. C₁₃H₁₅ClF₆NPW (549.53) calc.: C, 28.41; H, 2.75; Cl, 6.45; N, 2.55; W, 33.46%. FD-MS *m/z* 404 (K⁺).

4.2. [Cp₂WCl(CN^tBu)]PF₆ (**1b**)

Complex **1b** was prepared in a similar manner to **1a** from Cp₂WCl₂ (1.06 g, 2.75 mmol), ^tBuNC (0.32 ml, 2.83 mmol) and TlPF₆ (980 mg, 2.81 mmol). Orange-red crystals. Yield: 1.35 g (85%). Found: C, 31.06; H, 3.32; Cl, 6.24; N, 2.43; W, 31.11. C₁₅H₁₉ClF₆NPW (577.59) calc.: C, 31.19; H, 3.32; Cl, 6.14; N, 2.43; W, 31.83%.

4.3. [Cp₂W(CNEt)] (**2a**)

A suspension of **1a** (340 mg, 0.62 mmol) in 30 ml of THF was stirred for 30 min with 8.00 g of 1% Na/Hg (3.48 mmol Na). After addition of Et₂O the supernatant orange-brown solution was filtered and the volatiles were removed under reduced pressure. The residue was extracted with n-pentane and the filtered extract reduced in volume. Storage at -80°C overnight afforded brown crystals of **2a**, which were filtered off and dried *in vacuo*. Yield: 140 mg (61%). Found: C, 42.32; H, 4.23; N, 3.77; W, 49.06. C₁₃H₁₅NW (369.12) calc.: C, 42.30; H, 4.10; N, 3.79; W, 49.81%. EI-MS: *m/z* 369 (M⁺), 340 ([M – Et]⁺), 314 ([M – CNEt]⁺).

4.4. [Cp₂W(CN^tBu)] (**2b**)

Complex **2b** was prepared similarly to **2a** from **1b** (1.16 g, 2.01 mmol) and 1% Na/Hg (13.20 g, 5.75 mmol

Na). Brown, microcrystalline solid. Yield: 670 mg (84%). Found: C, 45.20; H, 4.92; N, 3.43; W, 45.64. $C_{15}H_{19}NW$ (397.17) calc.: C, 45.36; H, 4.82; N, 3.53; W, 46.29%.

4.5. $[Cp_2WEt(CNEt)]BF_4$ (**3a**)

A solution of **2a** (100 mg, 0.27 mmol) in 25 ml of THF was treated at -80°C with solid Et_3OBF_4 (50 mg, 0.26 mmol) and the mixture allowed to warm slowly to room temperature. A colour change from brown to yellow and a flocculent yellow precipitate separated within a few minutes. The suspension was stirred for 30 min and the volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2 and the filtered orange extract reduced in volume. Addition of Et_2O gave a yellow, microcrystalline precipitate which was filtered off, washed with Et_2O and dried *in vacuo*. Yield: 130 mg (quantitative). $C_{15}H_{20}BF_4NW$ (484.98). FD-MS: m/z 398 (K^+), 370 ($[K-C_2H_4]^+$).

4.6. $[Cp_2WMe(CN^tBu)]I$ (**4b**)

A solution of **2b** (120 mg, 0.30 mmol) in 20 ml of n-pentane was treated with MeI (0.019 ml, 0.31 mmol). During 30 min the colour changed from brown to yellow and a yellow solid separated. The solid was filtered off, washed with n-pentane, and dried *in vacuo*. Yield: 160 mg (98%). Found: C, 35.21; H, 4.11; I, 23.09; N, 2.53; W, 33.10. $C_{16}H_{22}INW$ (539.11) calc.: C, 35.65; H, 4.11; I, 23.54; N, 2.60; W, 34.10%. FD-MS: m/z 412 (K^+).

4.7. $[Cp_2WMe(CNMe)]I$ (**4c**)

Complex **4c** was prepared in a similar manner to **4b** from $[Cp_2W(CNMe)]$ (110 mg, 0.31 mmol) and MeI (0.02 ml, 0.32 mmol). Pale yellow solid. Yield: 150 mg (97%). Found: C, 32.50; H, 3.32; N, 2.82. $C_{13}H_{16}INW$ (497.03) calc.: C, 31.42; H, 3.24; N, 2.82%.

4.8. X-ray crystallography of **1a**

Suitable crystals were obtained by slow diffusion of Et_2O into a solution of **1a** in CH_2Cl_2 . Data were collected on a Phillips PW 1100 instrument (Mo K_α radiation, λ 0.71069 Å, graphite monochromator, room temperature). The crystal with dimensions 0.18, 0.25 and 0.42 mm was mounted in a Lindemann glass capillary. Crystal data: monoclinic, space group $P2_1/a$ (non-standard no. 14), a 14.957(3), b 10.413(2) and c 11.286(4) Å, β 106.05(2)°, $d_{\text{calcd.}}$ 2.161 g cm $^{-3}$, $Z = 4$, $\mu = 68.2$ cm $^{-1}$. Intensity data were collected by the $\theta/2\theta$ method; $6^\circ \leq 2\theta \leq 50^\circ$; 2958 independent reflections ($\pm h, k, l$), 2644 reflections considered as observed ($F_o > 3\sigma(F_o)$). The structure was solved by the Patterson-method. After the isotropic refinement an empirical correction for absorption was performed for

the F_o values [20]. Hydrogen atoms were then included at their calculated positions but not refined. Refinement [21] with anisotropic temperature factors for the heavy atoms gave R 0.044 and $R_w(F)$ 0.047. All calculations were performed on a PC with a 80386 CPU. Atomic coordinates (except those of H atoms) are listed in Table 5. Further details concerning the crystal structure analysis are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG) by quoting the depository number CSD-55609, the names of the authors, and the journal citation.

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