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Metal-centred C–C coupling of nitriles with 1-azaallyl ligands; synthesis and structure of β-diiminato complexes of tungsten

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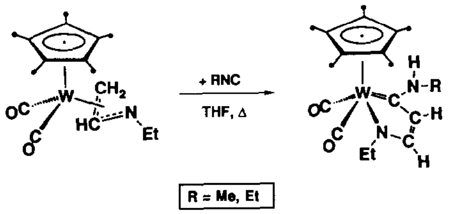
Abstract

An efficient procedure is reported for the synthesis of β-diiminato complexes starting from the readily accessible η^3-1-azaallyl complex $Cp^*(CO)_2W(\eta^3\text{-}CH_2 \text{⋯} CH \text{⋯} NEt)$ (**1**). The thermal reaction of **1** with nitriles RCN (R = Me, Ph) yields, by insertion of the nitrile into the metal–azaallyl–carbon bond, the β-diiminato complexes $Cp^*(CO)_2W[N(H)C(R)C(H)C(H)NEt]$ (**2a**: R = Me; **2b**: R = Ph). The solid-state structure of **2a** was determined by a single-crystal X-ray diffraction study. It reveals a "four-legged piano stool" complex composed of a $Cp^*(CO)_2W$-fragment and a N,N-chelated β-diiminato ligand. Bond distances and angles within the organic ligand indicate π-electron delocalization, as observed for the isoelectronic β-diketonates.

1. Introduction

1-azaallyl complexes of the alkali and alkaline earth metals are extremely useful reagents in organic synthesis, undergoing a variety of C–C bond-forming reactions with electrophiles [1]. The pioneering work of Wittig and Stork on controlled aldol condensation reactions and regioselective α-functionalizations of ketones involving 1-azaallyllithium and -magnesium compounds [2], or the use of lithiated chiral imines [3], hydrazones [4] and oxazolines [5] in asymmetric CC-coupling reactions are examples of the synthetic utility of these enolate equivalents in organic chemistry. By comparison, little is known about the reactivity of 1-azaallyl complexes of transition metals [6]. The reason for this is, that efficient methods have only recently been developed for the synthesis of this class of 1-heteroallyl complexes, involving the thermal isomerization of η^2-iminoacyl complexes [7], the insertion rearrangement of isocyanide alkyl complexes [7c,d,8], or the condensation of carbon-bound transition metal enolates with primary amines [9]. In this context we previously reported that the tungsten 1-azaallyl complex $Cp^*(CO)_2W(\eta^3\text{-}CH_2 \text{⋯} CH \text{⋯} NEt)$ (**1**) undergoes with alkylisocyanides a facile C–C bond forming reaction to give cyclic aminocarbene complexes (metallapyrroles) (eqn. (a)) and suggested that this coupling reaction is promoted by the facile η^3-η^1 slippage of the 1-azaallyl ligand [10]. This change in hapticity has been observed also in reactions of other transition-metal 1-heteroallyl complexes [11], and has been suggested to play a crucial role in several allylation reactions [12].



(a)

Continuing this work on metal-mediated C–C coupling reactions we describe below the synthesis of six-membered tungstenacycles by taking advantage of the facile C–C bond forming reaction of **1** with nitriles.

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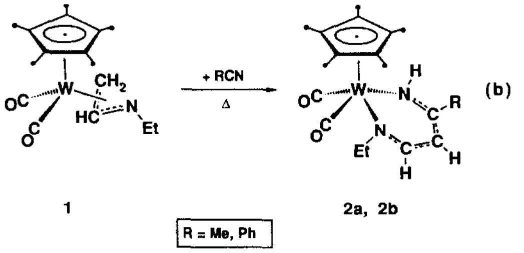
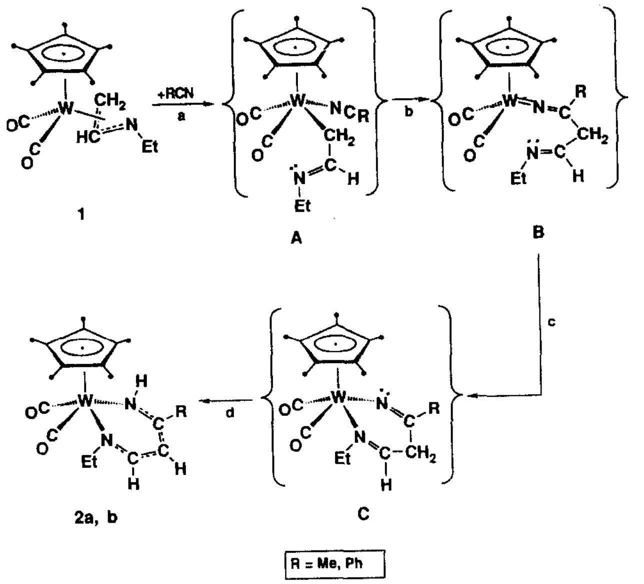
2. Results and discussion

When a solution of the η^3-1-azaallyl complex **1** in MeCN was refluxed for 24 h a clean C–C coupling reaction accompanied by a colour change from yellow to red occurred, leading to the β-diiminato complex **2a** (eqn. (b)).



Evidence for the quantitative conversion of **1** to **2a** was provided by the IR spectrum of the reaction solution, which revealed that the two strong ν(CO) absorptions of the starting material at 1923 and 1833 cm^{-1} had been replaced at the end of the reaction by the two strong ν(CO) absorptions of the product at 1898 and 1781 cm^{-1}. Complex **2a** was isolated as a red, slightly air-sensitive solid in 92% yield after removal of the solvent *in vacuo* and recrystallization of the residue from $\mathrm{Et_2O}$/n-pentane. Similarly, when complex **1** was heated in PhCN at 90°C a rapid reaction accompanied by a colour change from yellow to purple occurred, resulting in the formation of the β-diiminato complex **2b** (eqn. (b)). After work-up, compound **2b** was isolated as a purple, microcrystalline solid in 60% yield. The metallacycles decompose at 178 and 180°C, respectively when heated in a sealed capillary under nitrogen. They are soluble in $\mathrm{CH_2Cl_2}$, toluene and $\mathrm{Et_2O}$ but only sparingly soluble in n-pentane.

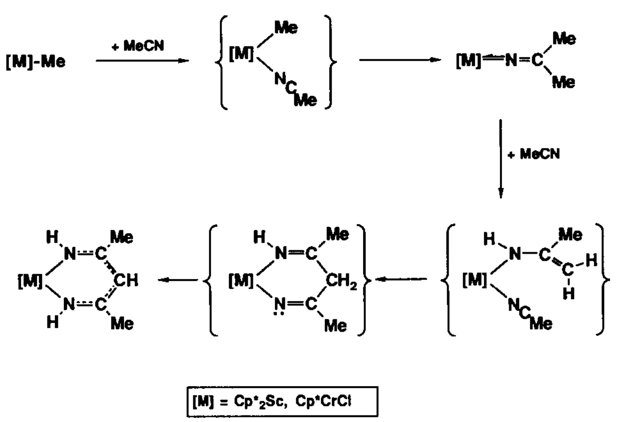
A possible mechanism for the formation of **2a** and **2b** is outlined in Scheme 1. In the first step the azaallyl nitrogen is displaced from the coordination sphere by the nitrile to give the carbon-bound tungsten enamide [(η^1-C)-1-azaallyl complex] **A** (Scheme 1, step a). There is precedent for such a transformation in the reaction of the η^3-1-oxaallyl complex $\mathrm{Cp(CO)_2W[\eta^3\text{-}CH_2{\cdots}C(OEt){\cdots}O]}$ with MeCN to give the carbon-bound tungsten enolate $\mathrm{Cp(CO)_2(MeCN)WCH_2CO_2Et}$, a complex closely related to A [11c]. Coordination of the nitrile through the nitrogen lone pair in **A** would be expected to induce polarization of the CN bond, encouraging in the next step a 1,3 alkyl shift from tungsten to the nitrile carbon to afford the 18e-alkylideneamido (ketimido) intermediate **B** (Scheme 1, step b). This reaction, which can alternatively be regarded as an insertion of the nitrile ligand in the tungsten–alkyl bond, is quite common for Group III and IV transition metal alkyl complexes and provides an easy route to isolable alkylideneamido complexes [13]. Moreover, stable molybdenum and tungsten alkylideneamido complexes of the type $\mathrm{Cp(CO)_2M(N{=}CRR')}$ (R, R′ = Ph, $p\text{-}\mathrm{C_6H_4Me}$, ^{t}Bu), which are analogous to **B**, have been previously obtained from the halo complexes $\mathrm{CpM(CO)_3X}$ (X = Cl, Br, I) upon treatment with lithium ketimides (LiN=CRR′) or ketiminosilanes ($\mathrm{Me_3SiN{=}CRR'}$) [14,15].



Scheme 1. Proposed mechanism for the formation of the β-diiminato complexes **2a** and **2b** from **1** and nitriles.

In the next step coordination of the remote imino group through the nitrogen lone pair would be expected to occur in **B** to afford the alkylideneamido (ketimido) intermediate **C**, which would finally isomerize by a 1,3-hydrogen shift (imine-enamine tautomerization) to the metallacycles **2a** and **2b** (Scheme 1, steps c and d). This isomerization process is probably promoted by the basic character of the ketimido nitrogen and the acidity of the methylene protons in **C**. A sequence of reaction steps similar to that suggested for the conversion of **B** to **2a** and **2b**, was previously proposed for the reaction of the transition-metal alkyl complexes $\mathrm{Cp^*_2ScMe}$ and $\mathrm{[Cp^*Cr(Cl)Me]_2}$ with RCN (R = Me, $p\text{-}\mathrm{C_6H_4OMe}$) to give the β-diiminato complexes $\mathrm{Cp^*_2Sc[N(H)C(R)C(H)C(R)NH]}$ (R = $p\text{-}\mathrm{C_6H_4}$-OMe) and $\mathrm{Cp^*Cr[N(H)C(Me)C(H)C(Me)NH]Cl}$, respectively (Scheme 2) [13b,16]. In addition, a 1,3-hydrogen shift analogous to that assumed in step d was previously observed in the Lewis-base promoted rearrangement of the alkali metal ketimides $\mathrm{[MN{=}C(^tBu)\text{-}{}^nBu]_n}$ to the η^3-1-azaallyl complexes $\mathrm{[(HMPT)_xM\{\eta^3\text{-}C(^nPr)H{\cdots}C(^tBu){\cdots}NH\}]_n}$ (M = Li; $x = 1$; M = Na; $x = 2$) [1f].

The reaction of **1** with nitriles to give β-diiminato complexes has an analogue in Main Group chemistry. Thus, Wittig *et al.* reported that the 1-azaallyllithium



Scheme 2. Proposed mechanism for the formation of transition-metal β-diiminato complexes from methyl complexes and acetonitrile.

compound Li[CH_2⋯C(H)⋯N^{c}hex] undergoes with RCN (R = Me, Ph, o-C_6H_4CN) a similar C–C coupling reaction to give a lithiated β-diketimine intermediate Li[N(H)C(Me)C(H)C(H)N^{c}hex], which after hydrolysis affords the enamine H_2NC(Me)=C(H)C(H)=N^{c}hex [17].

In the case of **1** this C–C coupling reaction is probably promoted by a η^3-η^1 slippage of the 1-azaallyl ligand facilitating coordination of the nucleophilic substrate. Whether this change in hapticity can be exploited in other metal-centred C–C coupling reactions is the focus of planned studies on the reactivity of η^3-1-azaallyl complexes.

2.1. Spectroscopic investigations

2.1.1. IR-spectra

The IR spectra support the proposed structures for the metallacycles **2a** and **2b** (Table 1). Thus both compounds exhibit in solution two strong, solvent-dependent ν(CO) absorptions, as observed for other "four legged piano-stool" complexes containing two mutually *cis*-oriented carbonyl ligands [7c,d,8b,10]. These absorptions appear at lower frequency than those for other structurally related Cp*W$(CO)_2$-derived metallacycles, reflecting the good σ-donor properties of the β-diiminato ligand [7c,d,8b,10]. In addition, both complexes are distinguished by two (**2a**) or three (**2b**) absorptions of medium intensity between 1500–1600 cm^{-1}, which are assigned to the ν(C⋯N) and ν(C⋯C) modes of the β-diiminato ligand, indicating extensive π-electron delocalization in this N,N-chelated ligand [18]. Similar absorptions have been previously reported for other β-diiminato complexes such as Cp*Cr[N(H)C(Me)C(H)C(Me)NH]Cl [ν(C⋯N) and ν(C⋯C) in KBr: 1573 and 1535 cm^{-1} [16] and Co[N(Et)C(H)C(H)C(Me)NEt]$_2$ [ν(C⋯N) and ν(C⋯C): 1575 and 1508 cm^{-1}] [19].

Finally the IR spectra of **2a** and **2b** in KBr exhibit a sharp absorption at 3346 and 3345 cm^{-1}, respectively, indicating the presence of an N–H bond (Table 1).

TABLE 1. ν(N–H), ν(C≡O) and ν(N⋯C⋯C⋯N)-absorptions of **2a** and **2b** in cm^{-1}; solvents: CH_2Cl_2 (a), MeCN (b), pentane (c), PhCN (d), toluene (e)

Complex	ν(N–H) (in KBr)	ν(C≡O)	ν(N⋯C⋯C⋯N)	solvent
2a	3346	1899vs, 1782s	1593w, 1538w	a
2a		1898vs, 1781s	1594w, 1537w	b
2a		1916vs, 1812s	1596w, 1532w	c
2b	3345	1900vs, 1785s	1591w, 1570w, 1534w	a
2b		1897vs, 1784s	1592w, 1570w, 1534w	d
2b		1906vs, 1798s	1591w, 1571w, 1531w	e

TABLE 2. ^{1}H NMR data for the complexes **2a** and **2b** in C_6D_6 or CD_2Cl_2 at +20°C; relative intensities and multiplicities in parentheses, coupling constants in Hz

Complex	NCH_2CH_3	CCH_3 CC_6H_5	$C_5(CH_3)_5$	NCH_2CH_3	CC*H*	N*H*	NC*H*	solvent
2a	1.07 (3, t) ^3J(HH) 7.3	1.33 (3, s)	1.72 (15, s)	3.18 (1, dq) $^2J(H_BH_A)$ 11.9 $^3J(H_BH_X)$ 7.3; 3.35 (1, dq) $^2J(H_AH_B)$ 11.9 $^3J(H_AH_X)$ 7.3	4.11 (1, dd) ^3J(HH) 6.7 ^4J(HH) 2.4	5.06 (1, br)	6.42 (1, d) ^3J(HH) 6.7	C_6D_6
2a	0.99 (3, t) ^3J(HH) 7.3	1.99 (3, s)	1.90 (15, s)	3.15 (1, dq) $^2J(H_BH_A)$ 11.9 $^3J(H_BH_X)$ 7.3; 3.70 (1, dq) $^2J(H_AH_B)$ 11.9 $^3J(H_AH_X)$ 7.3	4.34 (1, dd) ^3J(HH) 6.7 ^4J(HH) 3.0	5.35 (1, br)	6.77 (1, d) ^3J(HH) 6.7	CD_2Cl_2
2b	1.06 (3, t) ^3J(HH) 7.3	7.38–7.50 (5, m)	1.96 (15, s)	3.21 (1, dq) $^2J(H_BH_A)$ 11.9 $^3J(H_BH_X)$ 7.3; 3.77 (1, dq) $^2J(H_AH_B)$ 11.9 $^3J(H_AH_X)$ 7.3	4.77 (1, dd) ^3J(HH) 6.7 ^4J(HH) 3.0	5.70 (1, br)	6.99 (1, d) ^3J(HH) 6.7	CD_2Cl_2

2.1.2. ^1H NMR spectra

The ^1H NMR spectra are also consistent with the proposed structures for the metallacycles **2a** and **2b** (Table 2). Thus both complexes are chiral, possessing C_1 symmetry. Therefore the methylene protons of the N-bonded ethyl group are diastereotopic, giving rise to two well separate doublets of quartets as expected for the AB-part of an ABX_3 spin system [$^2J(H_AH_B) = 11.9$ Hz; $^3J(H_AH_x) = {^3J}(H_BH_X) = 7.3$ Hz) (Table 2) [20]. Furthermore the ^1H NMR spectra display two characteristic resonances for the non-equivalent methine groups at δ 4.34 and 6.77 (**2a** in CD_2Cl_2) and δ 4.77 and 6.99 (**2b**), the two methine protons being coupled to each other [$^3J(HH) = 6.7$ Hz]. The higher field methine resonance is split into a doublet of doublets owing to long range coupling of the CH with the NH proton [$^4J(HH) = 2.4$–3.0 Hz]. This resonance is therefore unequivocally assigned to the CH group next to the imino carbon. It is noteworthy that similar chemical shifts and coupling constants have been previously reported for the methine protons of other β-diiminato complexes such as $Zn[N(Et)C(Me)C(H)C(H)NEt]_2$ [δ(CH) 4.05 and 7.00; $^3J(HH) = 8$ Hz] [19] and $Cp^*{}_2Sc[N(H)C(R)C(H)C(R)NH]$ (R = p-C_6H_4OMe: δ(CH) 5.27; $^4J(HH) = 2$ Hz) [13b]. Finally the NH proton of the metallacycles gives rise to a broad resonance (unresolved doublet) at δ 5.35 (**2a** in CD_2Cl_2) and 5.70 (**2b**).

2.1.3. ^{13}C NMR spectra

Further support for the assigned structures of the β-diiminato complexes **2a** and **2b** is provided by the ^{13}C NMR spectra (Table 3). Both compounds are characterized by two low-field resonances for the imino carbons, at δ 159.0 and 164.9 (**2a**) and δ 159.9 and 164.6 (**2b**).

The higher field resonance (**2a**: δ 159.0; **2b**: δ 159.9) appears in the ^1H coupled ^{13}C-NMR spectra as a doublet, the $^1J(CH)$ coupling constant (156.2 Hz) being indicative of a $C(sp^2)$–H bond [21]. This resonance is therefore unequivocally assigned to the N-bonded CH group. In addition both metallacycles display one resonance at δ 95.9 (**2a**) and 95.1 (**2b**), which is assigned to the CH group attached to the imino carbon. As expected this resonance is split in the ^1H coupled ^{13}C-NMR spectra of **2a** and **2b** to a doublet, the $^1J(CH)$ coupling constant (162.3 and 163.0 Hz) again being indicative of a $C(sp^2)$–H bond. Similar chemical shifts have been previously reported for the ring carbons of the related β-diiminato complex $Cp^*{}_2Sc[N(H)C(R)C(H)C(R)NH]$ [R = p-C_6H_4OMe: δ(CH) 91.6, δ(CR) 168.5] [13b]. Finally, two different environments are observed for the inequivalent, mutually *cis*-oriented carbonyl ligands of the metallacycles, at δ 265.0 and 266.1 (**2a**) and δ 264.2 and 266.0 (**2b**).

2.2. Crystal structure of 2a

The solid state structure of **2a** was determined by a single crystal X-ray diffraction study. An ORTEP plot of the molecule, in one of the two orientations adopted, is given in Fig. 1 (for details of the structure see the Experimental section). Selected bond distances and angles are listed in Table 4 and fractional coordinates in Table 5. The crystal structure of **2a** is severely disordered (see Experimental section), and so discussion is restricted to the main structural features of **2a**.

The coordination geometry around the tungsten atom in **2a** can conveniently be described as distorted square pyramidal, with the Cp* ligand at the apex. The basal plane of the pyramid is defined by the carbonyl carbons C(7) and C(8) and the nitrogen atoms of the bidentate β-diiminato ligand N(1) and N(2), the maximal deviation of one of these atoms from the least squares plane being 0.5 pm. This plane is essentially parallel to the Cp* ring plane, the dihedral angle between the two planes being 1.3°. The orthogonal distance of the tungsten atom from the basal plane is 83.0 pm and that from the Cp* ring plane 203.1 pm. Both distances are close to those observed in other complexes containing a $Cp^*W(CO)_2$ fragment [7c,10,

TABLE 3. ^{13}C NMR data for the complexes **2a** and **2b** in CD_2Cl_2 at +20°C; coupling constants in Hz

Complex	$C_5(\mathit{C}H_3)_5$	$NCH_2\mathit{C}H_3$	$C\mathit{C}H_3$, $C\mathit{C}_6H_5$	$N\mathit{C}H_2CH_3$	$C\mathit{C}H$	$\mathit{C}_5(CH_3)_5$	$N\mathit{C}H$	CMe, CPh	$\mathit{C}O$
2a	11.2 $^1J(CH)$ 127.8	17.8 $^1J(CH)$ 127.0	27.7 $^1J(CH)$ 127.0	63.6 $^1J(CH)$ 134.3	95.9 $^1J(CH)$ 162.3	107.4	159.0 $^1J(CH)$ 156.2	164.9	265.0 266.1
2b	11.4 $^1J(CH)$ 127.6	17.8 $^1J(CH)$ 126.7	126.6 (C_m) $^1J(CH)$ 158.7; 128.9 (C_0) $^1J(CH)$ 161.7; 130.1 (C_p) $^1J(CH)$ 161.2; 141.7 (C_{ipso})	63.6 $^1J(CH)$ 134.3	95.1 $^1J(CH)$ 163.0	107.7	159.9 $^1J(CH)$ 156.2	164.6	264.2 266.0

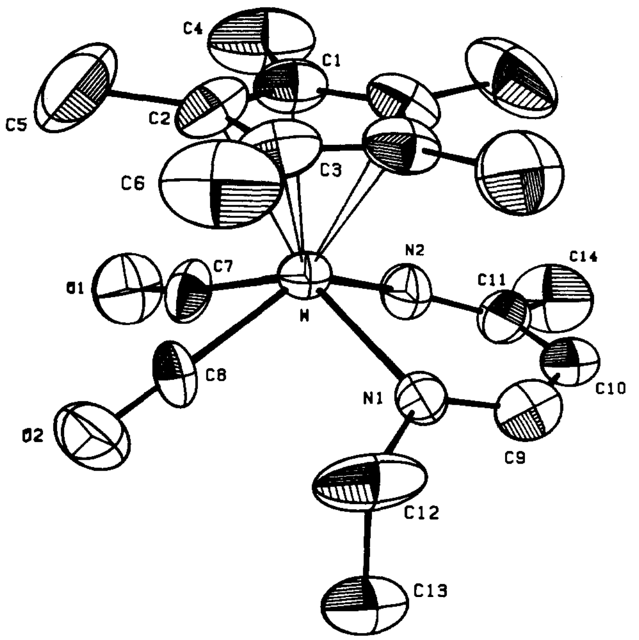


Fig. 1. ORTEP drawing of the molecular structure of **2a**. Hydrogen atoms are omitted for clarity reasons.

22]. The bite of the β-diiminato ligand [N(1)–W–N(2) = 83.3(3)°] in **2a** is larger than that of the cyclic aminocarbene ligand in the closely related five-membered metallacycle $Cp^*(CO)_2\overline{W[C(NHEt)C(H)C(H)N}Et]$ [10a]. This results in a more acute OC–W–CO bond angle in **2a** [C(7)–W–C(8) = 67.1(5)°] than that observed in the aminocarbene complex [OC–W–CO = 75.0(3)°] [10a]. The *trans* OC–W–L and OC–W–L′ bond angles [N(1)–W–C(7) = 131.9(4)°; N(2)–W–C(8) = 131.0(4)°] as well as the Cent–W–CO, Cent–W–L and Cent–W–L′ bond angles fall within the range observed for other "four-legged piano-stool" complexes of the type *cis*-$CpM(CO)_2LL'$ (Table 4) [23].

TABLE 4. Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **2a** [a]

W–C(1)	230(1)	N(2)–W–C(8)	131.0(4)
W–C(2)	236.5(7)	N(1)–W–C(8)	86.1(4)
W–C(3)	238.7(5)	N(2)–W–C(7)	85.5(3)
W–Cent	203	Cent–W–N(1)	111.0
W–C(7)	197.8(9)	Cent–W–N(2)	113.2
W–C(8)	200(1)	Cent–W–C(7)	116.4
W–N(1)	214.1(8)	Cent–W–C(8)	115.3
W–N(2)	208.7(8)	W–N(1)–C(9)	124.1(7)
N(1)–C(9)	131(1)	W–N(1)–C(12)	115.0(4)
C(9)–C(10)	142(2)	C(9)–N(1)–C(12)	120.9(8)
C(10)–C(11)	128(2)	W–N(2)–C(11)	130.9(7)
N(2)–C(11)	129(1)	N(2)–C(11)–C(10)	122.7(9)
C(11)–C(14)	153(2)	N(2)–C(11)–C(14)	120(1)
N(1)–W–N(2)	83.3(3)	N(1)–C(9)–C(10)	127(1)
C(7)–W–C(8)	67.1(5)	C(10)–C(11)–C(14)	117(1)
N(1)–W–C(7)	131.9(4)	C(9)–C(10)–C(11)	124(1)

[a] Cent denotes the centre of the pentamethylcyclopentadienyl ring.

TABLE 5. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms in **2a** [a]

Atom	x	y	z	B_{eq} (Å)^2
W	0.32290(2)	0.5000	0.76951(1)	2.17
O(1)	0.4903(7)	0.679(1)	0.9286(6)	4.80
O(2)	0.3831(8)	0.7865(9)	0.6907(8)	5.55
N(1)	0.3197(6)	0.3962(8)	0.6473(5)	2.37
N(2)	0.4131(7)	0.3229(8)	0.8354(6)	3.19
C(1)	0.2243(6)	0.5000	0.8566(5)	3.38
C(2)	0.1911(4)	0.6223(6)	0.7990(4)	3.81
C(3)	0.1453(4)	0.5752(7)	0.7064(3)	3.36
C(4)	0.271(1)	0.5000	0.9607(7)	6.55
C(5)	0.1959(7)	0.7810(9)	0.8277(8)	7.49
C(6)	0.0945(6)	0.672(1)	0.6234(5)	5.92
C(7)	0.4312(7)	0.615(1)	0.8651(8)	3.36
C(8)	0.3598(9)	0.6784(9)	0.7188(8)	3.77
C(9)	0.3317(8)	0.258(1)	0.6406(8)	3.39
C(10)	0.368(1)	0.156(1)	0.7141(9)	4.20
C(11)	0.4157(8)	0.194(1)	0.8062(8)	3.38
C(12)	0.2947(8)	0.5000	0.5595(6)	5.23
C(13)	0.3912(8)	0.5000	0.5410(7)	5.11
C(14)	0.472(1)	0.075(2)	0.875(1)	5.43

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\ \gamma)\beta_{12} + ac(\cos\ \beta)\beta_{12} + bc(\cos\ \alpha)\beta_{23}]$.

As expected the metal–carbonyl linkages are approximately linear [W–C(7)–O(1) = 172(1)°; W–C(8)–O(2) = 178(1)°] and the W–C_{CO} bonds [W–C(7) = 197.8(9) pm; W–C(8) = 200(1) pm] shorter than that of $W(CO)_6$[W–C = 205.8(3) pm] [24].

Chelation of the β-diiminato ligand through the nitrogen atoms N(1) and N(2) leads to a six-membered metallacycle. The W–N(1) and W–N(2) bond lengths of 214.1(8) and 208.7(8) pm are similar to those reported for other W^{II}–N(sp^2) bonds [10].

Extensive π electron delocalization along the NCCCN framework of the β-diiminato ligand is indicated by the C–N and C–C bond lengths [25,26] and the sum of the angles around N(1) and C(11) (360 and 359.7° respectively), showing sp^2-hybridization of these atoms. Additional evidence for π-electron delocalization is provided by the planarity of the NCCCN framework of the β-diiminato ligand the maximal deviation of one of these five atoms from the least squares plane being less than 6.1 pm. The tungsten atom is bent out of this plane by 63.6 pm towards the Cp* ligand, whereas the carbon atoms C(12) and C(14) are situated below this plane by 33.6 and 24.0 pm, respectively.

3. Experimental section

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane and Et_2O over

Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy; MeCN over P_2O_5 and K_2CO_3), distilled under nitrogen and stored over 4 Å (MeCN over 3 Å) molecular sieves prior to use.

Elemental analyses were performed by the Microanalytical laboratory of this department. IR spectra were recorded on a Nicolet 5DX and a Perkin Elmer 1650 FT spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in dry deoxygenated methylene-d_2-chloride or benzene-d_6 on a JEOL-JMX-GX 400 instrument. Chemical shifts were referenced to residual solvent signals (CD_2Cl_2 δ_H 5.32 and δ_C 53.8 ppm; C_6D_6 δ_H 7.15 and δ_C 128.0 ppm). Mass spectra were obtained with a Varian MAT 311A spectrometer; m/z values are relative to the ^{184}W isotope. Complex **1** was prepared as described previously [7c]. PhCN was dried over P_2O_5, and distilled under nitrogen prior to use.

3.1. *Cp*(CO)₂W[N(H)C(Me)C(H)C(H)NEt]* (**2a**)

A solution of 140 mg (0.31 mmol) of **1** in 50 ml of MeCN was refluxed for 24 h. Completion of the reaction was confirmed by IR spectroscopy. The resulting red solution was evaporated to dryness and the residue dissolved in Et_2O. The solution was freed from a small amount of a light brown impurity by filtration through a filter cannula and the filtrate evaporated to dryness *in vacuo*. The residue was recrystallized from Et_2O/n-pentane to give complex **2a** as a red, microcrystalline solid. M.p.: 178°C (dec.). Yield: 140 mg (92%). Found: C, 44.55; H, 5.46; N, 5.66. $C_{18}H_{26}N_2O_2W$ (486.26) calc.: C, 44.46; H, 5.39; N, 5.76%. EI-MS (70 eV): 486 $[M]^+$, 458 $[M - CO]^+$, 430 $[M - 2CO]^+$, 387 $[M - 2CO - NEt]^+$.

3.2. *Cp*(CO)₂W[N(H)C(Ph)C(H)C(H)NEt]* (**2b**)

A solution of 150 mg (0.34 mmol) of **1** in 15 ml of PhCN was heated at 100°C for 3 h until the reaction was complete. The resulting purple solution was worked up as described above for the synthesis of **2a** to give complex **2b** as a purple, microcrystalline solid. M.p.: 180°C (dec.). Yield: 110 mg (60%). Found: C, 49.83; H, 5.31; N, 4.88; W, 32.70. $C_{23}H_{28}N_2O_2W$ (548.33) calc.: C, 50.38; H, 5.15; N, 5.11; W, 33.53%. EI-MS (70 eV): 548 $[M]^+$, 520 $[M - CO]^+$, 492 $[M - 2CO]^+$, 449 $[M - 2CO - NEt]^+$.

3.3. *Structure determination of* **2a**

Suitable crystals were obtained as transparent dark-red parallelepipeds by cooling a saturated Et_2O/n-pentane solution of **2a** from room temperature to −78°C. A transparent single crystal with dimensions 0.31, 0.29 and 0.40 mm was mounted in a thin-walled glass capillary under argon. X-ray data were collected on a Enraf-Nonius CAD-4 four circle diffractometer with graphite monochromated Mo K_α radiation (λ = 71.073 pm) at 18°C. The space group was determined to be either the centric *C*2/*m* or the acentric *C*2 or *Cm* from the systematic absences. Data collection was carried out in the reduced triclinic cell, the data were then transformed to *C*2/*m* and averaged.

The subsequent solution and successful refinement of the structure was carried out in the centric space group *C*2/*m* despite serious disorder. In the space group *C*2/*m* the W, C(1), C(12) and C(13) atoms lie on a crystallographic mirror plane. The Cp* ligand is properly related by this mirror plane. The remaining ligands are disordered about this mirror plane such that there are two orientations of the ligands. In one orientation the CO ligands are on one side of the mirror plane, and the β-diiminato ligand [N(H)C(Me)-C(H)C(H)NEt] on the other side, with the ethyl group on the mirror plane.

The second conformation has every atom in the three disordered ligands on their respective opposite sides of the crystallographic mirror plane. The disorder places several atoms in close proximity to one another. To refine the model effectively it was necessary to refine the two carbonyls and the β-diiminato ligand in alternate least squares cycles. Due to the nature of the disorder it was also necessary seriously to consider the acentric space group *C*2 for which the mirror plane is not present (the mirror plane and therefore also the disorder would still be present in *Cm*). In *C*2 the Cp* ligand would not refine properly at all. Large correlations between parameters (related by a mirror plane in *C*2/*m*) and difference Fourier maps revealed the continued presence of disorder.

Unit cell constants were obtained by the least-square refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections at $\theta > 20°$ (a = 1398.8(6), b = 932.2(7) and c = 1576.9(9) pm, β 113.34(5)°; $V = 1888 \times 10^6$ pm^3, $Z = 4$, d_{calc} 1.71 g cm^{-3}). Intensity data for 3292 reflections (reduced cell) in the range $2° \leqslant 2\theta \leqslant 50°$ (h (9), k (±10), l (±18 reduced cell)) were collected by (ω-2θ) scans with a scan width of (0.80 + 0.35 tan θ).

The intensity data were corrected for Lorentz-polarization effects and for absorption (empirical correction, 9 reflections, μ = 64.1 cm^{-1}). After transforming the data to centred monoclinic, 1690 reflections were considered as observed ($F_o \geqslant 5\sigma(F_o)$). The structure was solved with SHELXS [27]. Due to the disorder, the hydrogen atoms were not included in the final refinement. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of R = 0.024 and R_w = 0.036. Final values of the positional parameters are given in Table 5. All calculations were performed on an AMDAHL 5890/300E computer using standard programs [27,28]. Neutral scattering parameters and anomalous dispersion effects were taken from ref. 29. The residual electron density maximum was 0.6 e^{-} $\AA^{-3}$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57069, the names of the authors and the journal citation.

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