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C–H activation of a MeN grouping in one of the CH₂NMe₂ *ortho* substituents of a NCN ‘pincer’ ligand in tungsten chemistry: X-ray structure of [WCl₂(NPh)(C₆H₃{CH₂NMeCH₂}-2-{CH₂NMe₂}-6)]

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Received 1 January 1999

Abstract

Reaction of the aryl and alkyl metal derivatives, [Li(C₆H₃(CH₂NMe₂)₂-2,6)]₂ (**1**), in situ prepared ‘Zn(C₆H₃(CH₂NMe₂)₂-2,6)₂’ (**2**), [Li(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})] (**3**) and [Zn(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})₂] (**4**), respectively, with either WOCl₄ or [W(NPh)Cl₄(Et₂O)] in Et₂O yielded insoluble products. According to elemental analysis and mass balance the adducts that were formed contained all of the starting compounds, including the respective Li and Zn salts eventually formed. However, when the arylzinc reagent **2** was reacted with [W(NPh)Cl₄(Et₂O)] in CH₂Cl₂, [WCl₂(NPh)(C₆H₃{CH₂N(Me)CH₂}-2-{CH₂NMe₂}-6)] (**6**) was formed, which was isolated in high yield. The single-crystal X-ray determination of **6** showed a NCN ligand that is η³-*mer*-*N,C,N*-bonded to the tungsten(VI) center via the (aryl)_{C_{ipso}} carbon and the two *ortho*-*N*-donor atoms. As one of the NCH₃ groups has undergone C–H activation, thus forming an azatungstacyclopropane ring, the NCN-pincer ligand is overall bonded to the tungsten centre as a tetradentate, η⁴-*N,C,N,C* coordinating dianionic ligand. The corresponding tungsten(VI) alkylidene complex [W(CH₂SiMe₃)(NPh)(C₆H₃{=CHN(Me)CH₂}-2-(CH₂NMe₂)-6)] (**7**) was generated by reaction of **6** with two equivalents of LiCH₂SiMe₃. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; C–H activation; Azatungstacyclopropane ring; *C,N*-chelate; Zinc

1. Introduction

Recently, we reported a number of Ta(V) [1] and W(VI) [2] alkylidenes that contain either an *ortho*-chelating bidentate mono aminoaryl or a bis *ortho*-chelating terdentate diaminoaryl ligand. The presence of a monoanionic, chelating *ortho*-amine ligand not only stabilizes the resulting aryl–Ta(V) and –W(VI) complexes but is also responsible for intramolecular

rearrangements [3] and interesting intramolecular aminomethyl C–H activation reactions [4]. Despite the stability of these complexes often high catalytic activity in ring-opening metathesis polymerization (ROMP) reactions with strained cyclic olefins like norbornene and dicyclopentadiene was found [2c].

To extend the number of tungsten complexes with the *C,N*-chelating manifold we investigated the synthesis of W(VI) complexes with aryl-, [C₆H₃(CH₂NMe₂)₂-2,6][–] (**I**), and alkyl-, [CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5}][–] (**II**), pincer ligands which, so far, have not been used in the field of W(VI) chemistry (see Fig. 1).

To generate the W(VI) alkylidene species containing these new ligands, [Li(C₆H₃(CH₂NMe₂)₂-2,6)]₂ (**1**) [5], in situ prepared ‘Zn(C₆H₃(CH₂NMe₂)₂-2,6)₂’ (**2**),

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[Li(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})] (3) [6], [Zn-(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})₂] (4) and [Me₃Si-CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5}] (5) [6], respectively, were reacted with [W(NPh)(CH₂SiMe₃)₃Cl] [7]. These reactions always resulted in the formation of mixtures of compounds, e.g. several W(VI) alkylidenes and the parent protonated ligands, which could not be separated by crystallization or washing procedures. Therefore, we decided to synthesize complexes such as [WOCl₃L] and [W(NPh)Cl₃L] (L = ligand I or II) first, and to generate the alkylidene moiety at a later stage. Here we report results obtained from reactions between 1–4 and WOCl₄ and [W(NPh)Cl₄(Et₂O)], respectively. The main products of these reactions were insoluble precipitates. However, products originating from unexpected C–H activation were also found when [W(NPh)Cl₄(Et₂O)] was reacted with 2 in CH₂Cl₂ yielding [WCl₂(NPh)(C₆H₃{CH₂N(Me)CH₂}-2-{CH₂Me₂}-6)] (6) and the corresponding alkylidene complex [W(CH₂SiMe₃)(NPh)(C₆H₃{=CHN(Me)CH₂}-2-(CH₂NMe₂)-6)] (7) after reaction with excess LiCH₂SiMe₃.

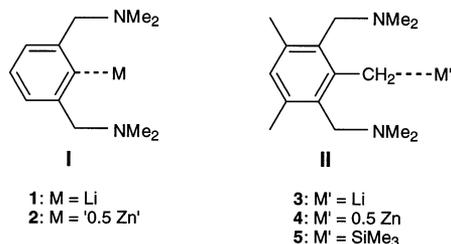


Fig. 1. The NCN-chelating ligands and the metalated complexes 1–5.

Table 1

Overview of the results of the reactions between the metal salts of the ligands and tungsten complexes (stoichiometry I/II: W = 1:1)

Compound	WOCl ₄ ^a	[W(NPh)Cl ₄ (Et ₂ O)] ^a
1	Purple/grey	Brown
0.5 Equiv. 2	Purple	Beige
3	Blue/grey ^b	Beige/green
0.5 Equiv. 4	Blue/grey ^c	Beige

^a Et₂O was used as solvent. Solutions or suspensions of 1–4 were carefully added to solutions of the W compounds at –78°C.

^b The elemental analysis of this product confirms the formation of an addition product of the lithium salt and W compound: Anal. Calc. for WOCl₄LiC₁₅H₂₅N₂ (%): C 30.96, H 4.33, N 4.81, Found: C 31.08, H 4.29, N 4.63. The Li salt could not be removed by extraction with THF.

^c The elemental analysis of this product confirms the formation of an addition product of the zinc salt and W compound: Anal. Calc. for W₂O₂Cl₈ZnC₃₀H₅₀N₄(%): C 29.65, H 4.15, N 4.61, Found: C 29.81, H 4.19, N 4.48.

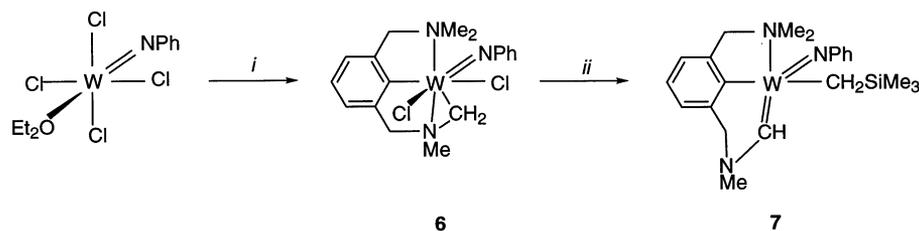
2. Results and discussion

The reactions between compounds 1–4 and WOCl₄ or [W(NPh)Cl₄(Et₂O)] in Et₂O give insoluble, intense colored solids (Table 1).

The mass balance and the elemental analysis of the complexes formed suggested that the products obtained from the reactions between 1–4 and WOCl₄ contained all of the starting compounds, as well as the lithium/zinc chloride eventually formed. Subsequent slurry reactions of the insoluble reaction products with Li–O–*t*-Bu to convert the blue/grey solids into more soluble *tert*-butoxy complexes failed. Furthermore, attempts to decomplex the probably strongly intermolecularly coordinated complexes by addition of coordinating bases like TMEDA and pyridine likewise did not result in the formation of soluble products.

The reactions of 1–4 with [W(NPh)Cl₄(Et₂O)] yielded brown/beige solutions at –78°C from which solids precipitated upon warming to room temperature (r.t.). The mass balance of the precipitates suggested that again complexes were formed which contain all the starting compounds, although in this case no satisfactory elemental analysis could be obtained. Also for these products additional slurry reactions with Li–O–*t*-Bu or the use of strongly coordinating bases failed to give secondary products with better solubility properties.

It was surprising to find that the reaction of 1 and 2 with WOCl₄ and [W(NPh)Cl₄(Et₂O)], respectively, yielded insoluble products, especially because the mono-(dimethylamino)methyl analogues [WO(C₆H₃(CH₂NMe₂)₂)Cl₃] and [W(NPh)(C₆H₃(CH₂NMe₂)₂)Cl₃] can be made in high yields (77%) by reaction of either WOCl₄ or [W(NPh)Cl₄(Et₂O)] with half an equivalent of [Zn(C₆H₃(CH₂NMe₂)₂)₂] [3a,b]. Apparently, the presence of an extra *ortho*-(dimethylamino)methyl functionality plays a crucial role. We have shown that the presence of this substituent can (i) cause the formation of coordination polymers [8]; (ii) accommodate an HCl functionality by formation of an ammonium molybdate in similar molybdenum(VI) chemistry [9]; (iii) accommodate ZnCl₂ as shown in tantalum(V) chemistry [1a] and (iv) play an important role in NCN rearrangement reactions involving the (aryl)C_{ipso}–M, aryl C–H and (NCH₃)C–M bonds [3]. In the present study the presence of the second *ortho*-(dimethylamino)methyl functionality possibly causes the formation of insoluble products by strong intermolecular coordination to the zinc/lithium salts. This insolubility prevented further purification and characterization of the products. For that reason a salt-free reaction route to the desired tungsten complexes was attempted, i.e. the reaction of the trimethylsilyl derivative of ligand II, [Me₃SiCH₂(C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5)] (5) with WOCl₄ and [W(NPh)Cl₄(Et₂O)], respectively, was un-



Scheme 1. Formation of the η^4 -N,C,N,C-pincer tungsten(VI) complex with the azatungstacyclopropane moiety. (i) In situ prepared 'Zn(C₆H₃(CH₂NMe₂)₂-2,6)₂' (**2**), CH₂Cl₂, r.t., ZnCl₂(NCNH), 95% yield. (ii) 2LiCH₂SiMe₃, 2LiCl, -SiMe₄, THF.

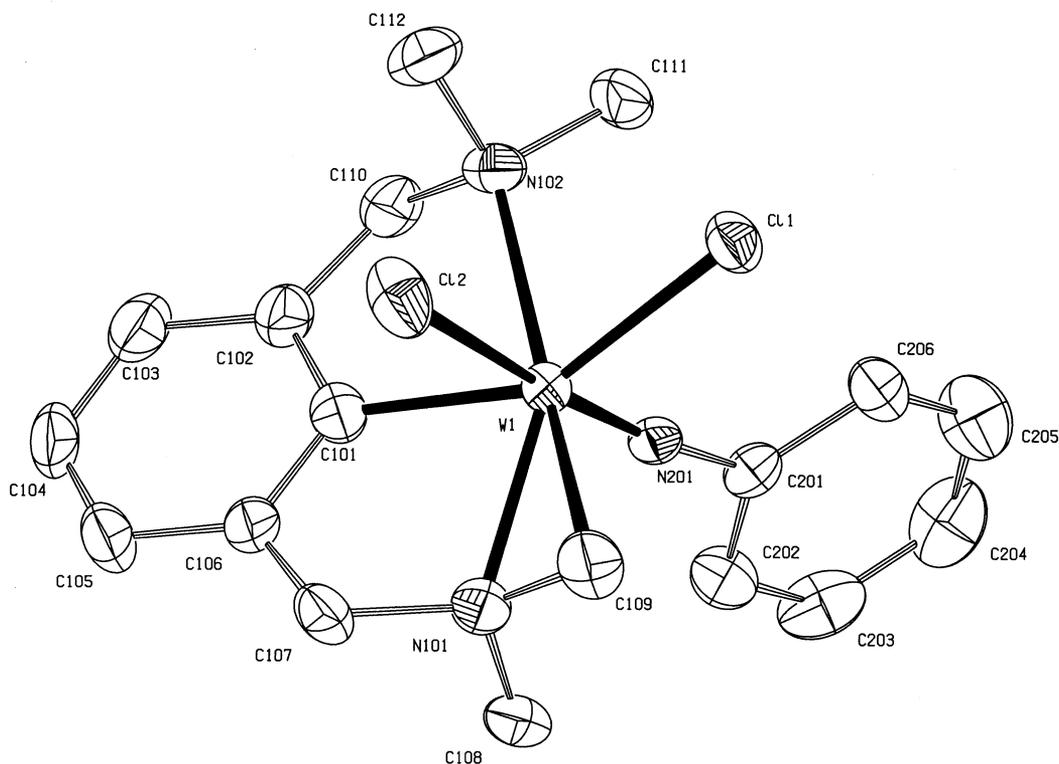


Fig. 2. Anisotropic displacement ellipsoid plot (ORTEP, at 50% probability level) of the molecular structure of **6**, together with the adopted numbering scheme. One disordered CH₂Cl₂ solvent molecule and hydrogen atoms have been omitted for clarity.

dertaken. Although this approach was applied with success in other cases (cf. Morrison et al. [10], Knotter et al. [11a] and Janssen et al. [11b]), we found that the reactions yielded complicated mixtures and were very slow, even when they were carried out under reflux conditions for several days in different solvents.

When one equivalent of **2** was added dropwise to a solution of [W(NPh)Cl₄(Et₂O)] in CH₂Cl₂ instead of Et₂O (stoichiometry I:W = 2:1), a yellow crystalline product could be isolated. It was identified by NMR, elemental analysis and single-crystal X-ray diffraction as the cyclometalated product [WCl₂(NPh)(C₆H₃{CH₂-N(Me)CH₂}-2-{CH₂NMe₂}-6)] (**6**) which was obviously formed by C–H activation of one of the NMe₂ substituents.

The ¹H NMR spectrum of **6** shows three singlet resonances (3.26, 3.13 and 2.84 ppm, CDCl₃) assigned

to the NMe groups and three AB patterns assigned to the methylene hydrogens of the CH₂N groups, i.e. these CH₂ hydrogens are diastereotopic. One set (5.32 and 5.10 ppm) shows ¹⁸³W–¹H coupling (²J_{WH} = 11.4 Hz). The diastereotopicity of the NMe₂ methyl groups establishes that intramolecular W–N coordination is rigid on the NMR timescale. The ¹³C–{¹H}-NMR data show three signals in the benzylic region (78.1, 78.0 and 76.1 ppm) and three signals with chemical shift values characteristic for NMe groups (60.3, 54.8 and 53.9 ppm). These NMR data are characteristic and consistent with the presence of a new NCH₂ unit formed as a result of C–H activation of one of the NMe groups of the [C₆H₃(CH₂NMe₂)₂-2,6][−] ligand (see Scheme 1).

The solid state structure was determined by a single-crystal X-ray determination and the molecular structure with the adopted numbering scheme is depicted in Fig.

2. Selected bond lengths and angles of **6** are given in Table 2.

The tungsten complex contains one imidophenyl group, two chloride atoms and an η^3 -*mer*-*N,C,N*-bonded pincer ligand with an azatungstacyclopropane unit as additional structural feature. The tungsten center has a pseudo-octahedral coordination geometry with mutually *cis*-positioned chloride atoms. The W–Cl(1) bond is slightly shorter than the W–Cl(2) bond with a Cl(1)–W–Cl(2) angle of almost 82°. The imido ligand is virtually linear (W–N–C = 173.6(6)°) and is positioned *trans* to Cl(2). The N(101)–W(1)–C(109) angle in the newly formed azatungstacyclopropane ring amounts to 39.2(2)°. The size of this angle is similar to those found in [TaCl₂{C₆H₄(CH(Me)N(Me)CH₂)-2}-(CH₂Ph)(THF)] (38.7(2)°) [4] and [TaCp*Cl₂{ η^3 -C₆H₄(CH₂N(Me)CH₂)-2}] (40.2(3)°) [12].

The tungsten alkylidene complex [W(CH₂SiMe₃)-(NPh)(C₆H₃{=CHN(Me)CH₂}-2-(CH₂NMe₂)-6)] (**7**) can be synthesized by reaction of **6** with two equivalents LiCH₂SiMe₃ in THF (see Scheme 1). Not only both chlorides are replaced but also subsequent alkylidene formation occurred. No information was obtained whether direct elimination occurred with LiCH₂SiMe₃ as a base or that first Cl substitution, followed by α -H elimination at the NCH₂-W(CH₂SiMe₃) unit takes place. The ¹H NMR spectrum of **7** in C₆D₆ shows the presence of an alkylidene proton at δ = 9.74 ppm with a large tungsten coupling (42.3 Hz), two AB patterns originating from the

diastereotopic CH₂N protons and an AB pattern which has been assigned to the CH₂Si protons. It is interesting to note that the alkylidene complex **7** was formed only when two equivalents of LiCH₂SiMe₃ were reacted with **6**. The use of other transmetallating agents containing α -H atoms, e.g. C₆H₅CH₂MgBr, C₆H₅CMe₂CH₂MgCl or MeMgCl in the place of LiCH₂SiMe₃, caused direct decomposition of **6** and formation of [C₆H₄(CH₂NMe₂)₂-1,3] (i.e. NCNH). No C–H activation of a CH₂SiMe₃ group which would lead to the formation of [W(=CHSiMe₃)(NPh)(C₆H₃{CH₂N(Me)CH₂}-2-{CH₂NMe₂}-6)], was observed. Compound **7** is very soluble in both polar and apolar solvents but decomposes within several hours with formation of paramagnetic tungsten complexes and the corresponding arene NCNH, which made complete characterization (¹³C-NMR, elemental analysis) complicated. Recently, Royo et al. reported a Ta(V) alkylidene complex which contains a similar Ta=CHNMe unit [12].

C–H activation of NMe groups is a common phenomenon in transition metal chemistry and has been reported by different groups, e.g. Abbenhuis et al. [4], De Castro et al. [12] and Bertuleit et al. [13]. The mechanistic pathway involved, i.e. via σ -bond metathesis or via a stepwise process involving metal–hydride complexes, is not clear yet, but C–H activation is facilitated when suitable anionic ligands are present. The use of two equivalents of the anionic NCN ligand **I** assures that two chloride ligands are replaced and that one of the C–H bonds in a NMe group is activated. The second NCN ligand is converted into the protonated NCN ligand NCNH. The resulting ZnCl₂ and NCNH form an insoluble adduct 'ZnCl₂(NCNH)' when the reaction is carried out in CH₂Cl₂. However, in the absence of CH₂Cl₂ as a solvent, the insoluble adduct which was also formed during the reaction of one equivalent of **2** with [W(NPh)Cl₄(Et₂O)] (see Table 1), is isolated as the main product. Most probably, the use of CH₂Cl₂ as a co-solvent assures that intermediate complexes such as [W(NPh)(NCN)Cl₃] and [W(NPh)(NCN)₂Cl₂] remain in solution. The spontaneous C–H bond activation at r.t. prevented the isolation of these complexes.

3. Experimental

All reactions were carried out under an atmosphere of dry N₂, using standard Schlenk techniques. All solvents were distilled from sodium under nitrogen, prior to use, except CH₂Cl₂, which was distilled from CaH₂. The ¹H- (300 MHz) and ¹³C-¹H- (75 MHz) NMR spectra were recorded in benzene-*d*₆ at r.t. unless otherwise indicated. Chemical shifts (in

Table 2
Selected bond lengths (Å)^a and angles (°)^a of [WCl₂(NPh)(C₆H₃-{CH₂N(Me)CH₂}-2-{CH₂NMe₂}-6)] (**6**)

<i>Bond lengths</i>	
W(1)–Cl(1)	2.4591(13)
W(1)–Cl(2)	2.5122(15)
W(1)–N(101)	2.142(5)
W(1)–N(102)	2.360(6)
W(1)–N(201)	1.745(4)
W(1)–C(101)	2.109(5)
W(1)–C(109)	2.160(7)
N(101)–C(109)	1.443(8)
N(201)–C(201)	1.390(7)
N(102)–C(111)	1.483(8)
N(102)–C(112)	1.487(8)
N(101)–C(108)	1.473(8)
<i>Bond angles</i>	
Cl(1)–W(1)–Cl(2)	81.94(5)
N(101)–W(1)–C(109)	39.2(2)
N(201)–W(1)–C(101)	101.96(19)
W(1)–N(201)–C(201)	173.6(6)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

ppm) are referenced to Me₄Si. Commercially available reagents were distilled prior to use. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The compounds WCl₄ [7]; [W(NPh)Cl₄(Et₂O)] [7]; [W(NPh)(CH₂SiMe₃)Cl] [7]; [Li(C₆H₃(CH₂NMe₂)₂-2,6)]₂ (**1**) [6]; [Li(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})] (**3**) [6]; [Me₃SiCH₂(C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5)] (**5**) [6] and LiCH₂SiMe₃ [14] were synthesized according to literature procedures.

3.1. *In situ* preparation of 'Zn(C₆H₃(CH₂NMe₂)₂-2,6)₂' (**2**)

To a solution of [Li(C₆H₃(CH₂NMe₂)₂-2,6)]₂ (1.07 g, 5.40 mmol) in Et₂O (50 ml) was added ZnCl₂ (0.37 g, 2.70 mmol) as a solid at once at r.t. After 2 h the suspension was centrifuged and the clear upper layer was separated from the white precipitate by decantation and was used as such.

3.2. [Zn(CH₂(C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5))]₂ (**4**)

To a solution of ZnCl₂ (1.27 g, 9.20 mmol) in Et₂O (50 ml) was added a suspension of [Li(CH₂{C₆H(CH₂NMe₂)₂-2,6-Me₂-3,5})] (4.45 g, 18.52 mmol) in Et₂O (50 ml) at -78°C. The reaction mixture was allowed to warm to r.t. and was stirred overnight. After 18 h, all volatiles were removed in vacuo. The residual white solid was extracted with pentane (2 × 100 ml) and the pentane layers were collected after centrifugation. All volatiles were removed in vacuo leaving a white solid (compound **4**; yield: 4.68 g (8.80 mmol, yield: 95%)) which was pure by NMR and elemental analysis. ¹H-NMR (δ): 6.58 (s, 1H, Ph-H_p), 3.40 (s, 4H, CH₂N), 2.30 (s, 6H, Me), 1.98 (s, 12H, NMe₂), 1.85 (s, 2H, ZnCH₂). ¹³C NMR (δ): 138.0, 133.1, 132.4 (C-Ph), 129.3 (*Cipso*), 59.4 (CH₂N), 45.9 (NMe₂), 19.8 (Me), 18.9 (ZnCH₂). *T*_{decomp} = 103°C. Anal. Calc. for C₃₀H₅₀N₄Zn: C, 67.22 (67.71); H, 9.35 (9.47); N, 10.50 (10.53).

3.3. [WCl₂(NPh)(C₆H₃{CH₂N(Me)CH₂}₂-2-{CH₂-NMe₂}₂-6)] (**6**)

A solution of **2** (5.40 mmol) in Et₂O (50 ml) was added over a period of 90 min to a CH₂Cl₂ (50 ml) solution of [W(NPh)Cl₄(Et₂O)] (1.31 g; 2.70 mmol) at r.t. After 18 h a yellowish precipitate was formed and was removed by centrifugation. The residual, clear orange solution was collected and all volatiles were removed in vacuo. The brown/yellow solid was extracted with THF (2 × 80 ml) and the clear solutions were collected after centrifugation. The THF layers were concentrated to 20 ml and upon addition of pentane (60 ml) a yellow precipitate appeared. The clear upper layer

was removed and the residual solids were washed with Et₂O (2 × 40 ml) and pentane (2 × 50 ml) and dried in vacuo (3 h, 60°C) leaving behind a yellow solid which was analysed as compound **6** (1.34 g, 2.56 mmol, 95%). Crystals suitable for X-ray analysis were grown in several weeks by putting a pentane layer on a CH₂Cl₂ solution of **6**. ¹H-NMR (δ, CDCl₃): 7.34 (m, 8H, Ar-H), 5.32 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 13.8 Hz), 5.10 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 13.8 Hz), 4.79 (d, 1H, WCH_AH_BN, ²J_{H_AH_B} = 13.6 Hz), 4.06 (d, 1H, WCH_AH_BN, ²J_{H_AH_B} = 13.6 Hz), 3.62 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 5.2 Hz), 3.43 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 5.2 Hz), 3.26 (s, 3H, NMe), 3.13 (s, 3H, NMe), 2.84 (s, 3H, NMe). ¹³C-NMR (d, CD₂Cl₂): 191 (*Cipso*), 153.7 (*Cipso* NAr), 144.8, 130.6, 130.0, 129.8, 128.6, 124.5 (aryl-C), 78.1, 78.0 (CH₂N), 76.1 (WCH₂), 60.3, 54.8, 53.9 (NMe). *T*_{melt} > 210°C. Anal. Calc. for C₁₈H₂₃N₃WCl₂: C, 40.08 (40.32); H, 4.44 (4.32); N, 7.70 (7.84).

3.4. [W(CH₂SiMe₃)(NPh){C₆H₃(=CHNMeCH₂)-2-(CH₂NMe₂)-6}] (**7**)

To a solution of **6** (0.30 g, 0.56 mmol) in THF (30 ml) was slowly added a solution of LiCH₂SiMe₃ (0.11 g, 1.12 mmol) in THF (10 ml) at -78 °C. After the addition was completed the solution was slowly (1 h) warmed to 0 °C. After 2 h all volatiles were removed in vacuo leaving behind a sticky yellow/orange material which was extracted with pentane (2 × 20 ml). The pentane layers were centrifuged and the clear upper layer was collected. All volatiles were removed in vacuo leaving behind (0.19 g, 0.35 mmol, 62%) of a yellow sticky solid, which slowly decomposes at r.t. yielding paramagnetic compounds and [C₆H₄(CH₂NMe₂)₂-2,6]. ¹H-NMR (δ, C6D6): 9.74 (s, 1H, W=CH, ²J_{W-H} = 42.3 Hz), 7.34–6.85 (m, 8H, Ar-H), 4.30 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 21.0 Hz), 4.21 (d, 1H, CH_AH_BN, ²J_{H_AH_B} = 9.1 Hz), 3.86 (d, 1H, WCH_AH_BN, ²J_{H_AH_B} = 21.0 Hz), 3.03 (d, 1H, WCH_AH_BN, ²J_{H_AH_B} = 9.1 Hz), 2.80 (s, 3H, NMe), 2.69 (s, 3H, NMe), 1.71 (s, 3H, NMe), 0.36 (s, 9H, SiMe₃), 0.18 (d, 1H, CH_AH_BSi, ²J_{H_AH_B} = 6.0 Hz), -0.18 (d, 1H, CH_AH_BSi, ²J_{H_AH_B} = 6.0 Hz).

3.5. Structure determination and refinement of **6**

X-ray data were collected on an Enraf-Nonius CAD4-T rotating anode diffractometer for a transparent, yellowish crystal glued on top of a glass fibre placed in a stream of N₂ at 150 K. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of 25 well-centered reflections (SET4) [15]. The unit-cell parameters were checked for the presence of higher lattice symmetry. Data were corrected for Lorentz po-

Table 3
Experimental data for the X-ray diffraction study of **6**

6	
Formula	C ₁₈ H ₂₃ N ₃ Cl ₂ W(CH ₂ Cl ₂)
Formula weight	621.09
Temperature (K)	150
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	12.0819(7)
<i>b</i> (Å)	12.8782(7)
<i>c</i> (Å)	16.1180(7)
β (°)	118.673(4)
Volume (Å ³)	2200.3(2)
<i>Z</i>	4
<i>d</i> _{calc.} (g cm ⁻³)	1.875
F(000) (electrons)	1208
μ (Mo–K α) (cm ⁻¹)	60.54
Crystal size (mm)	0.15 × 0.18 × 0.40
Radiation (Å)	Mo–K α (0.71073) ^a
θ^{\min} , θ^{\max} (°)	1.9, 27.5
Scan (ω -mode) (°)	0.54 + 0.35 tan(θ)
<i>h</i> , <i>k</i> , <i>l</i> (min, max)	–15, 9; –16, 16; –18, 20
Total/unique reflections	10 554, 5047
Observed reflections	3958 (<i>I</i> > 2.0 σ (<i>I</i>))
<i>N</i> _{ref} , <i>N</i> _{par}	5047, 221
<i>R</i> ; <i>wR</i> ; <i>S</i> ^b	0.0344; 0.0774; 1.03
Weight (<i>w</i> ⁻¹) ^c	$\sigma^2(F_o^2) + (0.0353P)^2 + 1.81P$
Min., max. resd. dens. (e Å ⁻³)	–1.96, 2.12

^a Graphite monochromated.

^b $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

^c $P = (\max(F_o^2, 0) + 2F_c^2) / 3$.

larisation effects. An empirical absorption correction was applied (PLATON/DELABS) [16]. The structure was solved by Direct methods and subsequent difference Fourier techniques (SHELXS86) [17]. The structure was found to contain voids filled with disordered CH₂Cl₂. Their contribution to the structure factors in the least squares refinement was taken into account by back-fourier transformation using PLATON/SQUEEZE [16]. Refinement on *F*² was carried out by full-matrix least-squares techniques (SHELXL93) [18] using no observance criterion. Hydrogen atoms were included on calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom. Weights were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography [19]. Geometrical calculations and illustrations were performed with PLATON [16]. All calculations were performed on a DECstation 5000 cluster. Crystal data and numerical details of the structure determinations and refinements are collected

in Table 3, final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **6** are given in Table 4. Selected geometrical details of the structure are listed in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 113892 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-0336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

J.A.M.B. gratefully acknowledges financial support by Dutch Technology Foundation (STW) with financial aid from the Council for Chemical Science of the Netherlands/Organization for Scientific Research (NWO/CW). Dr G.J.M. Gruter (DSM Research), Dr

Table 4

Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **6**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²) ^a
W(1)	0.23858(2)	0.30092(2)	0.35704(1)	0.0247(1)
Cl(1)	0.27789(13)	0.48026(10)	0.41675(9)	0.0338(4)
Cl(2)	0.06416(14)	0.38762(11)	0.21471(10)	0.0463(4)
N(101)	0.1067(4)	0.1905(4)	0.3581(3)	0.0361(14)
N(102)	0.3775(5)	0.3450(4)	0.2981(3)	0.0339(14)
N(201)	0.3652(4)	0.2482(3)	0.4575(3)	0.0256(12)
C(101)	0.2098(5)	0.1888(4)	0.2532(3)	0.0307(16)
C(102)	0.2918(6)	0.1794(4)	0.2167(4)	0.0362(17)
C(102)	0.2918(6)	0.1794(4)	0.2167(4)	0.0362(17)
C(103)	0.2640(7)	0.1104(5)	0.1417(4)	0.0440(19)
C(104)	0.1555(7)	0.0510(5)	0.1073(4)	0.049(2)
C(105)	0.0733(6)	0.0597(5)	0.1434(4)	0.0459(19)
C(106)	0.1001(6)	0.1291(4)	0.2173(4)	0.0372(19)
C(107)	0.0168(5)	0.1538(5)	0.2602(4)	0.0397(17)
C(108)	0.1559(6)	0.1010(5)	0.4226(4)	0.046(2)
C(109)	0.0924(5)	0.2872(5)	0.3972(4)	0.0415(19)
C(110)	0.4078(6)	0.2452(5)	0.2652(4)	0.0395(19)
C(111)	0.4986(5)	0.3903(5)	0.3701(4)	0.0418(17)
C(112)	0.3228(7)	0.4178(5)	0.2165(4)	0.048(2)
C(201)	0.4707(5)	0.2176(4)	0.5405(4)	0.0274(14)
C(202)	0.4957(5)	0.1124(4)	0.5644(4)	0.0369(17)
C(203)	0.6012(6)	0.837(5)	0.6463(4)	0.047(2)
C(204)	0.6848(6)	0.1601(6)	0.7046(5)	0.053(2)
C(205)	0.6597(6)	0.2622(6)	0.6807(5)	0.051(2)
C(206)	0.5543(5)	0.2924(4)	0.5991(4)	0.0360(17)

^a *U*_{eq} is one-third of the trace of the orthogonalized *U* tensor.

J.A.M. van Beek, Dr F.H. van der Steen (Shell, Amsterdam) and Dr A.A. van der Huizen (Shell) are thanked for fruitful discussions.

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