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Journal of Organometallic Chemistry 689 (2004) 1771–1779
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and selective silylation of ω-hydroxy functionalized (η^2-alkenyl)carbene complexes of chromium(0) and tungsten(0) Part 11. The chemistry of metallacyclic alkenylcarbene complexes ☆

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Received 28 November 2003; accepted 2 February 2004

Abstract

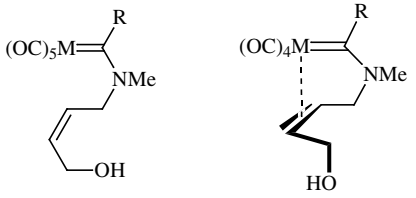
Tungsten(0) carbene complexes of the type $(OC)_5W{=}C(NMeCH_2CH{=}CHCH_2OH)R$ **2** (R = Me: **2a**; R = Ph: **2b**) were generated by aminolysis of $(OC)_5W{=}C(OMe)R$ with *cis*-$NHMeCH_2CH{=}CHCH_2OH$. Like their Cr-congeners **1**, complexes **2** exist at room temperature as mixtures of *Z*- and *E*-isomers with regard to the C–N bond. The metallacyclic complexes $(OC)_4W{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OH)R$ (**4**) were obtained in good yields upon photo-decarbonylation of **2**. Deprotonation/silylation of the complexes $(OC)_4M{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OH)Me$ (M = Cr: **3a**; M = W: **4a**) with one equivalent of ^{n}BuLi/Me_3SiCl gave $(OC)_4M{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OSiMe_3)CH_3$ (M = Cr: **5**; M = W: **6**), whereas with two equivalents of ^{n}BuLi/Me_3SiCl complexes $(OC)_4M{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OSiMe_3)CH_2SiMe_3$ (M = Cr: **7**; M = W: **8**) were formed. Hydrolysis of the latter yielded selectively $(OC)_4M{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OH)CH_2SiMe_3$ (M = Cr: **9**; M = W: **10**). The complexes **1**–**10** were analyzed in solution by one- and two-dimensional NMR spectroscopy (^1H, ^{13}C, ^{29}Si, $^1H/^1H$ COSY, $^1H/^1H$ NOESY, $^{13}C/^1H$ HETCOR).

Keywords: Chromium; Tungsten; Carbene complexes; η^2-Alkene; *Z*-/*E*-isomers; NMR

1. Introduction

Carbene-(η^2-alkene) complexes of group VI transition metals are pivotal though elusive intermediates in important C–C bond forming processes such as the cyclopropanation [2] and the metathesis [3] or polymerization of olefins. Stable metallacyclic derivatives having the alkene ligand tethered to the carbene carbon atom are interesting model systems for the study of these reactions. Their reactivity and selectivity is dependent not only of the nature of the central metal, the ancillary ligands and the substituents on the carbene and alkene ligands, but also of the geometry restraints imposed by the tether length (i.e. the ring size) [4–6]. For a detailed study of their chemistry flexible ways to further functionalize them are needed.

Herein, we describe the synthesis of tungstacyclic carbene complexes **4** and of their non-chelated precursors **2** which feature a terminal hydroxy residue amenable to selective silylation. The NMR spectra of complexes **2**, **4**, of the known [7] chromium analogues **1** and **3**, and of silyl derivatives of **3a** and **4a** are discussed as reflecting minor structural differences.



R	M: Cr	M: W
Me	**1a**	**2a**
Ph	**1b**	**2b**

R	M: Cr	M: W
Me	**3a**	**4a**
Ph	**3b**	**4b**

☆ For part 10, see [1].

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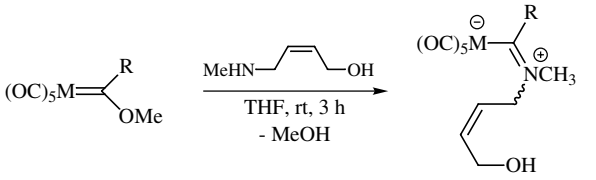
doi:10.1016/j.jorganchem.2004.02.032

2. Results and discussion

2.1. Synthesis of aminocarbene complexes $(OC)_5M{=}C(NMeCH_2CH{=}CHCH_2OH)R$ 1 and 2

Complexes of types **1** and **2** can be prepared by aminolysis of methoxycarbene complexes, $(OC)_5M{=}C(OMe)R$ (M = Cr, W; R = Me, Ph) with 1-methylamino-but-(2*Z*)-en-4-ol in THF (Scheme 1). Purification of the products and removal of excess amine is possible by column chromatography. The products are yellow air-sensitive oils. Interestingly, chelated complexes **3** and **4**, respectively, were also formed as by-products (<7–8%) under these conditions. This parallels Dvorak's [6] findings for the reaction of *N*,*N*-diallylbenzamide with



	M	R	[%]	*Z*/*E*
1a	Cr	Me	60	4:1
1b	Cr	Ph	54	1:5
2a	W	Me	67	3:1
2b	W	Ph	63	1:1

Scheme 1.

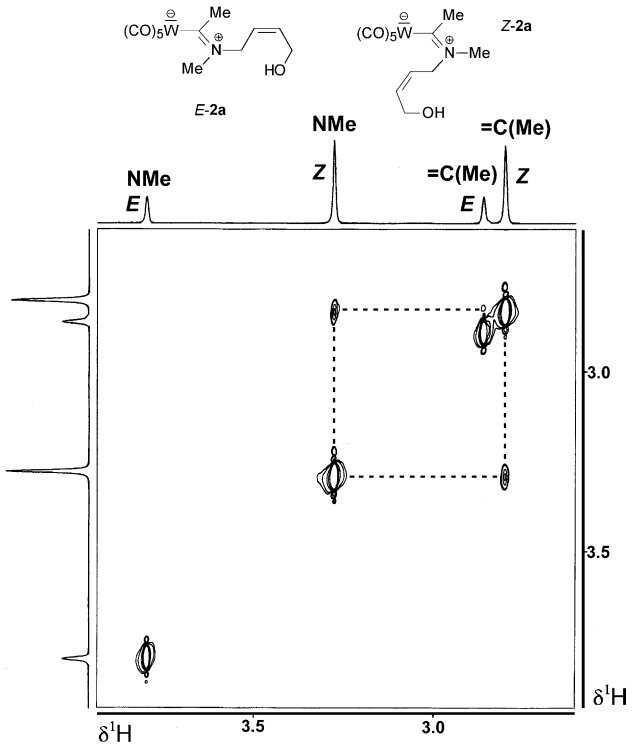


Fig. 1. $^1H/^1H$ NOESY spectrum for the methyl groups of the *Z*–*E*-isomers of **2a** (saturated solution in acetone-d_6, run at 23 °C): NOE between the NMe– and the =C(Me)– groups of the *Z*-isomer (***Z*-2a**).

$Na_2Cr(CO)_5$ producing the corresponding metallacyclic (η^2-alkene)carbene complexes even predominantly.

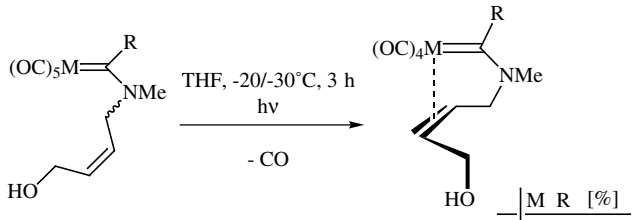
Compounds **1** and **2** were formed at room temperature as mixtures of *Z*- and *E*-isomers with regard to the formal C–N double bond, but contrary to earlier reports on similar systems [8], with the *Z*-isomer being the major component, except for **1b**. The isomers are clearly distinguishable in the ^1H and ^{13}C NMR spectra and unambiguously assignable by means of one- and two-dimensional NOE experiments. These, for instance, revealed a spatial proximity of the two vicinal methyl groups in the case of **2a** (Fig. 1).

2.2. Synthesis of chelated(η^2-alkenyl)carbene complexes $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)R$ 3 and 4

Irradiation of the complexes **1** at −30 °C or **2** at −20 °C in THF led to loss of a terminal CO ligand and ligation of the alkene in the side-chain to give complexes **3** and **4**, respectively. Upon inert gas column chromatography on silica gel 60 these eluted as a yellow band (second) with diethyl ether to leave bright yellow (**3a**, **4a**) or dark yellow (**3b**, **4b**) air-sensitive solids in yields ranging from ca. 70–80% upon evaporation (Scheme 2).

2.3. Synthesis of the silylated complexes $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)Me$ (M = Cr: 5; M = W: 6), $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2\ OSiMe_3)CH_2SiMe_3$ (M = Cr: 7; M = W: 8) and $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)CH_2SiMe_3$ (M = Cr: 9; M = W: 10)

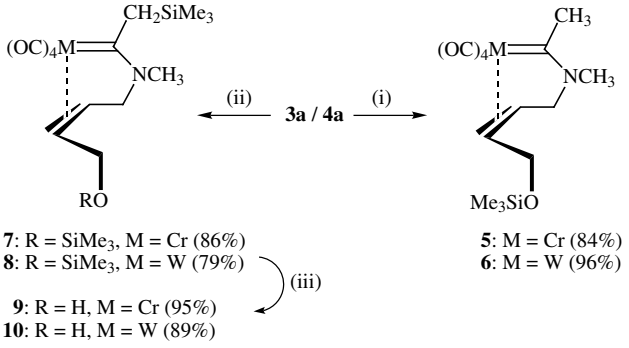
The silylation of α-methyl residues in aminocarbene complexes to give synthetically useful [(α-silylalkyl)]carbene complexes has been reported earlier [9]. We now found, that the hydroxy and the methyl protons of the complexes **3a** and **4a**, respectively, can be abstracted stepwise with one and two equivalents of ^{n}BuLi at low temperatures, due to their different acidities. The reaction with one equivalent of ^{n}BuLi followed by treatment with Me_3SiCl gave exclusively the O-silylated compounds **5** or **6**, respectively, as air-sensitive, yellow solids, separable from LiCl by simple filtration.



	M	R	[%]
3a	Cr	Me	81
3b	Cr	Ph	70
4a	W	Me	69
4b	W	Ph	75

Scheme 2.

Consecutive addition of two equivalents each of ^{n}BuLi and Me_3SiCl to complexes **3a** or **4a** led to replacement of both acidic hydrogens (–O*H* and M=C–C*H*H_2) with silyl groups furnishing the oily orange product complexes **7** or **8**, respectively. They were also easily purified by a simple filtration and were hydrolyzed to leave the respective ω-hydroxy functionalized (η^2-alkenyl)carbene complexes **9** and **10** as air-sensitive, yellow powders in excellent yields. Scheme 3 summarizes these regioselective terminal silylations of complexes **3a** and **4a**. Products **5**–**10** were characterized spectroscopically including ^{29}Si NMR.



Scheme 3. Reagents and conditions: (i) ^{n}BuLi (1 eq.), THF, −78 °C; then Me_3SiCl (1 eq.), −78 °C → r.t.; (ii) ^{n}BuLi (2 eq.), THF, −78 °C; then Me_3SiCl (2 eq.), −78 °C → r.t.; (iii) H_2O, Et_2O, r.t.

2.4. NMR spectroscopic results

^{13}C NMR data of **1** and **2** (all isomers) are given in Table 1, those of **3** and **4** in Table 2. The ^{29}Si and ^{13}C NMR data of the compounds **5**–**10** are summarized in Table 3.

As to the ^{1}H and ^{13}C NMR spectra of tungsten complex **2a**, *Z*- and *E*-isomers with respect to the C–N bond are present in a 3:1 ratio. As expected [8], the carbene carbon atoms of aminocarbene complexes **1** (ca. 270 ppm) and **2** (ca. 250 ppm) peak at significantly higher field when compared to the starting methoxycarbene complexes (Cr: 350–360 ppm; W: 320–330 ppm) owing to N being a better electron donor than O [10]. The assignment of the two isomers of **1** and **2** was based on 1D and 2D NOE experiments with the α-Me and the N-Me (for **1a**, **2a**) or the α-Me and *ortho*-phenyl-H (for **1b**, **2b**) groups. In the ^{1}H/^{1}H NOESY spectrum of **2a** (Fig. 1), for example, only the C-attached methyl group of the major isomer

Table 1
^{13}C data[a,b] of complexes ***Z***-/***E***-**1** and ***Z***-/***E***-**2** (**1a**: $Z/E \approx 4/1$, **1b**: $Z/E \approx 1/5$, **2a**: $Z/E \approx 3/1$, **2b**: $Z/E \approx 1/1$)

	δ^{13}C(M=C)	δ^{13}C(=CH–)	δ^{13}C(NMe)	δ^{13}C(R)	δ^{13}C(–CH_2–)	δ^{13}C(CO)
Z-**1a**	269.8 (s)	125.2 (s) 136.4 (s)	40.7 (s)	40.5 (s, C^{Me})	58.7 (s, C^{NCH_2}) 64.4 (s, C^{CH_2OH})	218.7 (s) 224.5 (s)
E-**1a**	270.5 (s)	123.6 (s) 135.7 (s)	53.6 (s)	38.5 (s, C^{Me})	51.5 (s, C^{NCH_2}) 58.6 (s, C^{CH_2OH})	218.9 (s) 226.5 (s)
Z-**2a**	252.0 (s) [92.1]	124.9 (s) 136.0 (s)	42.3 (s)	38.9 (s, C^{Me}) [5.8]	58.7 (s, C^{NCH_2}) 65.9 (s, C^{CH_2OH})	199.3 (s) [127.1] 204.2 (s) [127.2]
E-**2a**	252.6 (s) [91.9]	123.4 (s) 135.4 (s)	53.8 (s)	41.5 (s, C^{Me}) [6.0]	52.0 (s, C^{NCH_2}) 58.4 (s, C^{CH_2OH})	199.7 (s) [127.2] 204.3 (s) [127.1]
Z-**1b**	271.2 (s)	124.7 (s) 137.0 (s)	43.5 (s)	119.8 (s, C^m) 127.7 (s, C^p) 129.1 (s, C^o) 154.2 (s, C^i)	58.3 (s, C^{NCH_2}) 58.8 (s, C^{CH_2OH})	218.0 (s) 224.8 (s)
E-**1b**	272.1 (s)	124.1 (s) 136.3 (s)	49.2 (s)	120.2 (s, C^m) 126.5 (s, C^p) 129.2 (s, C^o) 153.5 (s, C^i)	56.3 (s, C^{NCH_2}) 62.0 (s, C^{CH_2OH})	218.2 (s) 224.9 (s)
Z-**2b**	254.6 (s) [91.5]	124.5 (s) 136.7 (s)	41.7 (s)	120.0 (s, C^m) 126.7 (s, C^p) 129.0 (s, C^o) 153.6 (s, C^i) [8.2]	58.9 (s, C^{NCH_2}) 64.0 (s, C^{CH_2OH})	199.1 (s) [127.6] 204.9 (s) [127.2]
E-**2b**	255.4 (s) [91.2]	124.0 (s) 135.9 (s)	51.3 (s)	120.3 (s, C^m) 126.6 (s, C^p) 128.8 (s, C^o) 154.2 (s, C^i) [9.1]	54.6 (s, C^{NCH_2}) 58.2 (s, C^{CH_2OH})	198.9 (s) [127.3] 204.6 (s) [127.0]

[a] Solutions in acetone-d_6 (saturated; at 23 °C).
[b] Coupling constants $^nJ(^{183}W, ^{13}C)$ are given in brackets (±0.1 Hz).

Table 2
^{13}C data[a,b] of complexes **3** and **4**

	$\delta^{13}C$(M=C)	$\delta^{13}C$(=CH–)	$\delta^{13}C$(NMe)	$\delta^{13}C$(R^1)	$\delta^{13}C$(–CH_2–)	$\delta^{13}C$(CO)
3a	275.4 (s)	76.5 (s) 87.6 (s)	38.5 (s)	33.5 (s, C^{Me})	61.6 (s, C^{NCH_2}) 62.0 (s, C^{CH_2OH})	224.9 (s) 226.0 (s) 227.0 (s) 233.9 (s)
3b	276.3 (s)	77.7 (s) 89.4 (s)	41.5 (s)	120.7 (s, C^m) 127.1 (s, C^p) 129.4 (s, C^o) 149.7 (s, C^i)	60.8 (s, C^{CH_2OH}) 62.2 (s, C^{NCH_2})	223.9 (s) 225.0 (s) 228.2 (s) 231.7 (s)
4a	255.6 (s) [85.0]	72.9 (s) [7.0] 83.6 (s) [7.9]	38.7 (s)	35.9 (s, C^{Me}) [9.3]	62.1 (s, C^{NCH_2}) 62.6 (s, C^{CH_2OH})	203.8 (s) [121.4] 205.6 (s) [126.2] 210.6 (s) [130.2] 214.3 (s) [153.9]
4b	257.4 (s) [84.0]	73.4 (s) [6.4] 84.5 (s) [8.4]	41.4 (s)	121.3 (s, C^m) 127.4 (s, C^p) 129.0 (s, C^o) 150.6 (s, C^i) [5.8]	61.0 (s, C^{CH_2OH}) 62.6 (s, C^{NCH_2})	203.3 (s) [122.6] 205.2 (s) [127.5] 211.2 (s) [130.0] 211.7 (s) [154.5]

[a] Solutions in acetone-d_6 (saturated; at 23 °C).
[b] Coupling constants $^nJ(^{183}W, ^{13}C)$ are given in brackets (±0.1 Hz).

Table 3
^{29}Si and ^{13}C NMR data [a,b,c] of complexes **5**–**10**

	$\delta^{29}Si$	$\delta^{13}C$(M=C)	$\delta^{13}C$(=CH–)	$\delta^{13}C$(NMe)	$\delta^{13}C$(R)	$\delta^{13}C$(–CH_2–)	$\delta^{13}C$(CO)	$\delta^{13}C$($OSiMe_3$)
5	17.8 (s)	275.7 (s)	76.6 (s) 87.0 (s)	38.6 (s)	33.6 (s, C^{Me})	61.8 (s, C^{CH_2O}) 62.7 (s, C^{NCH_2})	224.7 (s) 225.6 (s) 226.9 (s) 233.8 (s)	−0.3 (s) {58.8}
6	17.5 (s)	255.6 (s) [85.0]	72.6 (s) [7.1] 82.6 (s) [8.2]	38.6 (s)	35.8 (s, C^{Me}) [9.3]	62.1 (s, C^{NCH_2}) 63.1 (s, C^{CH_2O})	203.5 (s) [121.7] 205.2 (s) [126.2] 210.3 (s) [129.8] 214.0 (s) [153.5]	−0.2 (s) {58.7}
7	3.4 (s) 17.8 (s)	275.4 (s)	77.6 (s) 88.8 (s)	39.1 (s)	0.4 (s, C^{SiMe_3}) {52.2} 42.8 (s, C^{CH_2}) {36.6}	61.2 (s, C^{CH_2O}) 62.4 (s, C^{NCH_2})	224.2 (s) 224.3 (s) 227.1 (s) 233.5 (s)	−0.2 (s) {58.6}
8	3.5 (s)17.5 (s)	254.9 (s) [84.4]	74.0 (s) [6.9] 84.4 (s) [8.7]	39.1 (s)	0.2 (s, C^{SiMe_3}) {52.1} 44.6 (s, C^{CH_2}) {36.8} [7.5]	61.4 (s, C^{CH_2O}) 63.0 (s, C^{NCH_2})	203.2 (s) [124.6] 204.2 (s) [126.2] 209.4 (s) [127.9]213.4 (s) [154.7]	−0.2 (s) {58.7}
9	3.4 (s)	275.4 (s)	78.1 (s) 90.0 (s)	39.4 (s)	0.6 (s, C^{SiMe_3}) {52.0} 43.0 (s, C^{CH_2}) {34.6}	61.3 (s, C^{CH_2OH}) 62.0 (s, C^{NCH_2})	224.8 (s) 224.9 (s) 227.5 (s) 234.0 (s)	–
10	3.5 (s)	254.9 (s) [84.6]	74.6 (s) [6.7] 85.7 (s) [8.5]	39.0 (s)	0.2 (s, C^{SiMe_3}) {51.4} 44.5 (s, C^{CH_2}) {34.9} [7.0]	61.2 (s, C^{CH_2O}) 62.3 (s, C^{NCH_2})	203.2 (s) [124.5] 204.2 (s) [125.2] 209.4 (s) [127.6]213.4 (s) [155.6]	–

[a] Solutions in acetone-d_6 (saturated; at 23 °C).
[b] Coupling constants $^nJ(^{183}W, ^{13}C)$ are given in [ ] (±0.1 Hz).
[c] Coupling constants $^2J(^{29}Si, ^{13}C)$ are given in { } (±0.1 Hz).

gave rise to strong cross-peaks with the N-methyl group, thus indicating this isomer to be the *Z*-form. The $^1J(^{183}W, ^{13}C)$ coupling constants observable in the ^{13}C NMR spectra of the tungsten complexes **2** are in the typical range of magnitude [11], e.g. ca. 92 Hz for the carbene carbon atoms.

Upon coordination of the alkene, the respective ^{13}C NMR spectra change as expected for planar-chiral

chelated alkene–carbene complexes. The resonance signals of the olefinic carbon atoms of complexes **3**–**10** experience a conspicuous highfield shift of almost 50 ppm originating from d → π* backdonation of electron density from the metal to the alkene ligand. For compounds **4**, **6**, **8**, and **10** these signals also show a small $^1J(^{183}W, ^{13}C)$ coupling of 6.5–8.7 Hz (Fig. 2). This speaks for a relatively intact olefin bond rather than a metallacyclopropane structure which typically exhibits couplings $^1J(^{183}W, ^{13}C)$ of 10–12 Hz [12]. As a result of alkene ligation and a lowered symmetry, the four terminal CO ligands are no longer equivalent in these complexes. Accordingly, four distinct signals with different $^1J(^{183}W, ^{13}C)$ couplings are observed (e.g. Fig. 2 for **6**), one of which is significantly greater (ca. 155 Hz)

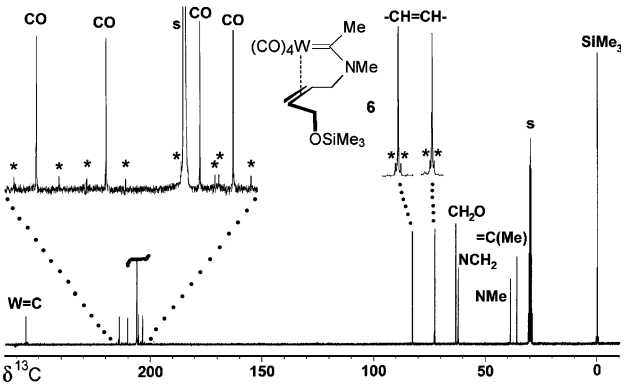


Fig. 2. 63.9 MHz ^{13}C NMR spectrum of **6** (saturated solution in acetone-d_6 (**s**), recorded at 23 °C).

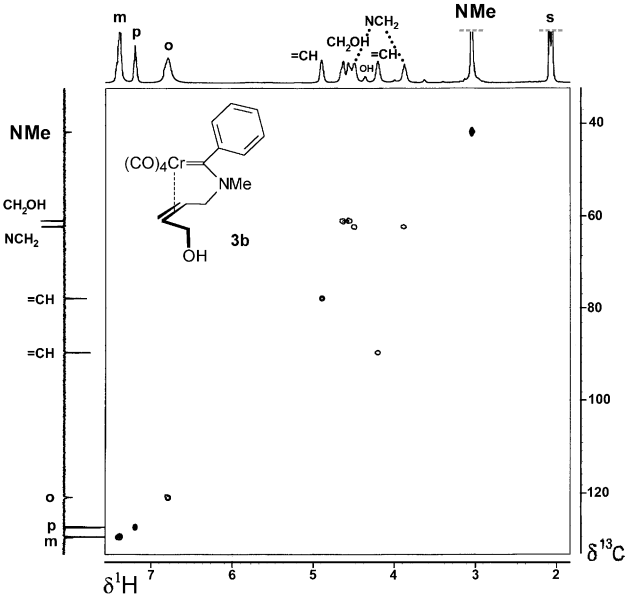


Fig. 3. $^{13}C/^1H$ HETCOR NMR (HMQC) spectrum of **3b** (saturated solution in acetone-d_6, recorded at 23 °C): highfield shift of the coordinated alkene carbon signals and diastereotopicity of the protons of the NCH_2– and the CH_2OH– groups.

than the other three (120–130 Hz) and thus is likely to belong to the CO opposite to the alkene ligand [12–14]. Finally, a complete assignment of all signals in the ^1H and ^{13}C NMR spectra was achieved by means of 2D $^1H/^1H$ COSY and $^{13}C/^1H$ HETCOR (HMQC, HMBC) spectroscopy. The protons of the methylene groups next to the alkene, for example, were found diastereotopic, each giving rise to two cross-peaks in the $^1H/^{13}C$ HETCOR NMR (HMQC) which is shown for **3b** in Fig. 3.

^{29}Si NMR spectroscopy was conducive to tracing the silylating reactions. The spectra of the monosilylated compounds **5** and **6** showed just one singlet at ca. 17.5 ppm, a shift typical of $OSiMe_3$ groups [15]. A further signal (1:1 ratio) at higher field (ca. 3.5 ppm) cropped up following the second deprotonation/silylation cycle to give **7** and **8**. It can be assigned to the CH_2SiMe_3 group attached to the carbene carbon atom [15] and it persisted upon hydrolysis to give complexes **9** and **10** while the one ascribed to the $OSiMe_3$ moiety vanished.

3. Conclusions

We have demonstrated the generality of the Fischer aminolysis/photodecarbonylation protocol for the synthesis of chelated (η^2-alkene)carbene complexes of group VI transition metals from methoxycarbene complexes and 1-methylamino-but-(2*Z*)-en-4-ol. Although the intermediate non-chelated carbene complexes **1**, **2** were comprised of varying proportions of *Z*- and *E*-isomers, their irradiation furnished the same good yields of the respective metallacycles **3**, **4**, probably due to a photo-induced isomerization at some stage along the decarbonylation-chelation process. We also found a convenient deprotonation/silylation (/hydrolysis) procedure for the selective synthesis of derivatives monosilylated either at the O- (**5**, **6**) or the C-terminus (**9**, **10**) of the metallacycle. Work is in progress now to build up alkynyl side-armed (η^2-alkene)carbene complexes amenable to thermal domino insertion-cyclopropanation reactions leading to metal-free oligo-azacycles.

4. Experimental

4.1. General information

Preparation and handling of all compounds was carried out in an atmosphere of dry argon, and absolute solvents were used throughout. Starting materials were prepared according to the literature procedures, e.g. $(OC)_5M{=}C(OMe)R$ (M = Cr, W; R = Me, Ph) [16], $HOCH_2CH{=}CHCH_2NHMe$ [7] or were used as purchased, without further purification, e.g. $HOCH_2CH{=}CHCH_2OH$, $SOCl_2$, NH_2Me, $M(CO)_6$ (M = Cr, W), MeLi

(1.6 M in hexane), PhLi (2.0 M in hexane) and Me_3OBF_4.

NMR spectroscopy: Bruker ARX 250, DRX 300 and DRX 500 (^1H, ^{13}C); direct single pulse runs, or in the case of the ^{29}Si and some ^{13}C NMR spectra by using the refocused INEPT pulse sequence with ^1H decoupling [17], based on $^2J(^{29}Si, ^1H) \approx 7$ Hz or $^nJ(^{13}C, ^1H) \approx 3$–5 Hz. ^1H NMR spectra were recorded in acetone-d_6 at 23 °C; chemical shifts are given with respect to Me_4Si [δ ^1H (CD_3COCD_2H) = 2.04; δ ^{13}C (CD_3COCD_3) = 29.8, 204.0]. IR spectra: Perkin–Elmer, Spectrum 2000 FTIR. EI-MS: Finnigan MAT 8500 (ionization energy 70eV). Elemental analysis: Heraeus Mikromat C–H–N. *hv*: Hanau TQ 150 mercury vapour lamp.

4.2. Synthesis of $(OC)_5M{=}C(NMeCH_2CH{=}CHCH_2OH)R$ (**1**) [7] and (**2**) – general procedure

1-Methylamino-but-(2*Z*)-en-4-ol (1.01 g, 10.0 mmol), dissolved in THF (10 ml), was added at once to a solution of $(CO)_5M{=}C(OMe)R$ (M = Cr, W; R = Me: 5.2 mmol, Ph: 3.4 mmol) in THF (50 ml). The mixture was stirred at room temperature for 3 h (for **1**) or 4 h (for **2**). After removal of the solvent in vacuo, the remainder was chromatographed (silica gel 60, diethyl ether). The eluate (first fraction) was brought to dryness leaving the products as yellow oils.

4.2.1. *Z-/E-*$(OC)_5Cr{=}C(NMeCH_2CH{=}CHCH_2OH)Me$ (**1a**) [7]

$Z/E \approx 4/1$; yield: 996 mg (60%), $C_{12}H_{13}CrNO_6$. ^1H NMR (250 MHz): ***Z*-1a**: $\delta = 2.75$ (s, 3H, H^{Me}), 3.34 (s, 3H, H^{NMe}), 4.02 (br, 1H, H^{OH}), 4.32 (d, 2H, $^3J = 5.6$ Hz, H^{NCH_2}), 5.04 (d, 2H, $^3J = 6.7$ Hz, H^{CH_2OH}), 5.54 (m, 1H, H^{CH}), 5.94 (m, 1H, H^{CH}); ***E*-1a**: $\delta = 2.81$ (s, 3H, H^{Me}), 3.90 (s, 3H, H^{NMe}), 3.97 (br, 1H, H^{OH}), 4.18 (d, 2H, $^3J = 5.5$ Hz, H^{NCH_2}), 4.57 (d, 2H, $^3J = 6.6$ Hz, H^{CH_2OH}), 5.48 (m, 1H, H^{CH}), 5.79 (m, 1H, H^{CH}).

4.2.2. *Z-/E-*$(OC)_5Cr{=}C(NMeCH_2CH{=}CHCH_2OH)Ph$ (**1b**) [7]

$Z/E \approx 1/5$; yield: 700 mg (54%), $C_{17}H_{15}CrNO_6$. ^1H NMR (300 MHz): ***E*-1b**: $\delta = 3.83$ (br, 1H, H^{OH}), 3.99 (d, 2H, $^3J = 5.4$ Hz, H^{NCH_2}), 4.00 (s, 3H, H^{NMe}), 4.21 (d, 2H, $^3J = 7.3$ Hz, H^{CH_2OH}), 5.44 (m, 1H, H^{CH}), 5.79 (m, 1H, H^{CH}), 6.86 (m, 2H, H^p), 7.18 (m, 1H, H^o), 7.40 (m, 2H, H^m); ***Z*-1b**: $\delta = 3.06$ (s, 3H, H^{NMe}), 3.86 (br, 1H, H^{OH}), 4.35 (d, 2H, $^3J = 5.8$ Hz, H^{NCH_2}), 5.19 (d, 2H, $^3J = 6.7$ Hz, H^{CH_2OH}), 5.73 (m, 1H, H^{CH}), 6.02 (m, 1H, H^{CH}), 6.83 (m, 2H, H^p), 7.19 (m, 1H, H^o), 7.43 (m, 2H, H^m).

4.2.3. *Z-/E-*$(OC)_5W{=}C(NMeCH_2CH{=}CHCH_2OH)Me$ (**2a**)

$Z/E \approx 3/1$; yield: 1.57 g (67%), $C_{12}H_{13}NO_6W$. ^1H NMR (300 MHz): ***Z*-2a**: $\delta = 2.79$ (s, 3H, H^{Me}), 3.27 (s, 3H, H^{NMe}), 4.14 (br, 1H, H^{OH}), 4.29 (d, 2H, $^3J = 6.1$ Hz, H^{NCH_2}), 4.93 (d, 2H, $^3J = 6.9$ Hz, H^{CH_2OH}), 5.53 (m, 1H, H^{CH}), 5.94 (m, 1H, H^{CH}); ***E*-2a**: $\delta = 2.85$ (s, 3H, H^{Me}), 3.79 (s, 3H, H^{NMe}), 4.18 (br, 1H, H^{OH}), 4.23 (d, 2H, $^3J = 6.1$ Hz, H^{NCH_2}), 4.49 (d, 2H, $^3J = 6.8$ Hz, H^{CH_2OH}), 5.51 (m, 1H, H^{CH}), 5.86 (m, 1H, H^{CH}). IR(ATR): $\nu = 3334$ cm^{-1} [br, ν(OH)], 2060/2022/1966/1853 [$\nu(W(CO)_5)$], 1521 [ν(C=C)]. EI-MS: m/z (%) = 451 (29) [M^+], 423 (13) [M^+–CO], 395 (5) [M^+–2CO], 367 (2) [M^+–3CO], 339 (20) [M^+–4CO], 311 (80) [M^+–5CO], 280 (100), 268 (46), 253 (36), 238 (49), 225 (24), 210 (28), 182 (15), 114 (8), 82 (18), 71 (21). Anal. Calc. for $C_{12}H_{13}NO_6W$ (451.1) C, 31.55; H, 2.90; N 3.10. Found: C, 31.64; H, 2.98; N, 3.03%.

4.2.4. *Z-/E-*$(OC)_5W{=}C(NMeCH_2CH{=}CHCH_2OH)Ph$ (**2b**)

$Z/E \approx 1/1$; yield: 1.10 g (63%), $C_{17}H_{15}NO_6W$. ^1H NMR (300 MHz): ***Z*-2b**: $\delta = 3.05$ (s, 3H, H^{NMe}), 4.04 (t, 1H, $^3J = 5.3$ Hz, H^{OH}), 4.35 (m, 2H, H^{NCH_2}), 5.15 (m, 2H, H^{CH_2OH}), 5.71 (m, 1H, H^{CH}), 6.03 (m, 1H, H^{CH}), 6.91 (m, 2H, H^m), 7.18 (m, 1H, H^p), 7.44 (m, 2H, H^o); ***E*-2b**: $\delta = 3.80$ (t, 1H, $^3J = 5.4$ Hz, H^{OH}), 3.95 (s, 3H, H^{NMe}), 4.00 (m, 2H, H^{NCH_2}), 4.23 (m, 2H, H^{CH_2OH}), 5.47 (m, 1H, H^{CH}), 5.80 (m, 1H, H^{CH}), 6.91 (m, 2H, H^m), 7.18 (m, 1H, H^p), 7.44 (m, 2H, H^o). IR(ATR): $\nu = 3344$ cm^{-1} [br, (OH)], 2060/1973/1869 [$\nu(W(CO)_5)$], 1522 [ν(C=C)]. EI-MS: m/z (%) = 513 (20) [M^+], 485 (26) [M^+–CO], 457 (14) [M^+–2CO], 429 (9) [M^+–3CO], 401 (43) [M^+–4CO], 373 (100) [M^+–5CO], 342 (81), 302 (60), 275 (71), 259 (39), 214 (43), 210 (28), 184 (36), 170 (81), 118 (96), 91 (76) [$C_7H_7^+$], 77 (93) [$C_6H_6^+$]. Anal. Calc. for $C_{17}H_{15}NO_6W$ (513.2) C, 39.79; H, 2.95; N 2.73. Found: C, 39.63; H, 2.88; N, 2.61%.

4.3. Synthesis of $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)R$ (**3**) [7] and (**4**) – general procedure

A solution of $(OC)_5M{=}C(NMeCH_2CH{=}CHCH_2OH)R$ **1** or **2**, respectively (3.0 mmol) in THF (80 ml) was irradiated at −20 °C (**2**) or −30 °C (**1**) for 2–3 h with a Heraeus low-pressure mercury lamp (150 W) in an apparatus described elsewhere [7]. The solvent was removed in vacuo and the resulting residue was chromatographed on silica gel. The second yellow fraction eluted with diethyl ether was collected and brought to dryness. The solid crude products were repeatedly washed with pentane and dried in high vacuum, to give bright (**3a**, **4a**) or dark (**3b**, **4b**) yellow powders.

4.3.1. $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)Me$ (**3a**) [7]

Yield: 708 mg (81%); m.p. 71 °C (dec.), $C_{11}H_{13}CrNO_5$. ^1H NMR (250 MHz): $\delta = 2.38$ (s, 3H, H^{Me}), 3.23 (s, 3H, H^{NMe}), 3.52 (m, 1H, H^{NCH_2}), 4.02 (m,

1H, H^{CH}), 4.22 (br, 1H, H^{OH}), 4.32 (m, 1H, H^{NCH_2}), 4.44 (m, 1H, H^{CH_2OH}), 4.47 (m, 1H, H^{CH_2OH}), 4.67 (m, 1H, H^{CH}).

4.3.2. $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)Ph$ (**3b**) [7]

Yield: 742 mg (70%); m.p. 73 °C (dec.), $C_{16}H_{15}CrNO_5$. ^1H NMR (300 MHz): $\delta = 3.04$ (s, 3H, H^{Me}), 3.86 (m, 1H, H^{NCH_2}), 4.19 (m, 1H, H^{CH}), 4.36 (t, 1H, $^3J = 10.2$ Hz, H^{OH}), 4.48 (m, 1H, H^{NCH_2}), 4.57 (m, 1H, H^{CH_2OH}), 4.61 (m, 1H, H^{CH_2OH}), 4.88 (m, 1H, H^{CH}), 6.79 (m, 2H, H^o), 7.19 (m, 1H, H^p), 7.38 (m, 2H, H^m).

4.3.3. $(OC)_4W{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)Me$ (**4a**)

Yield: 876 mg (69%); m.p. 89 °C (dec.), $C_{11}H_{13}NO_5W$. ^1H NMR (300 MHz): $\delta = 2.52$ (s, 3H, H^{Me}), 3.27 (s, 3H, H^{NMe}), 3.83 (m, 1H, H^{NCH_2}), 4.18 (br, 1H, H^{OH}), 4.29 (m, 1H, H^{CH}), 4.39 (m, 1H, H^{NCH_2}), 4.44 (m, 1H, H^{CH_2OH}), 4.69 (m, 1H, H^{CH_2OH}), 4.80 (m, 1H, H^{CH}). IR (ATR): $\nu = 3371$ cm^{-1} [ν(OH)], 2015/1967/1867/1838 [ν(W(CO)$_4$)], 1529 [ν(C=C)]. EI-MS: m/z (%) = 423 (18) [M^+], 395 (7) [M^+–CO], 367 (5) [M^+–2CO], 339 (17) [M^+–3CO], 311 (28) [M^+–4CO], 281 (42), 266 (38), 229 (100), 91 (52), 58 (7), 43 (42), 28 (4) [CO^+]. Anal. Calc. for $C_{11}H_{13}NO_5W$ (423.1) C, 31.22; H, 3.10; N 3.31. Found: C, 31.24; H, 3.08; N, 3.23%.

4.3.4. $(OC)_4W{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)Ph$ (**4b**)

Yield: 1.09 g (75%); m.p. 82 °C (dec.), $C_{16}H_{15}NO_5W$. ^1H NMR (300 MHz): $\delta = 3.10$ (s, 3H, H^{Me}), 4.10 (m, 1H, H^{NCH_2}), 4.33 (t, 1H, $^3J = 10.7$ Hz, H^{OH}), 4.43 (m, 1H, H^{CH}), 4.50 (m, 1H, H^{NCH_2}), 4.57 (m, 1H, H^{CH_2OH}), 4.89 (m, 1H, H^{CH_2OH}), 5.03 (m, 1H, H^{CH}), 6.89 (m, 2H, H^o), 7.21 (m, 1H, H^p), 7.40 (m, 2H, H^m). IR (ATR): $\nu = 3358$ cm^{-1} [ν(OH)], 2014/1971/1843 [ν(W(CO)$_4$)], 1537 [ν(C=C)]. EI-MS: m/z (%) = 485 (7) [M^+], 457 (3) [M^+–CO], 429 (2) [M^+–2CO], 401 (8) [M^+–3CO], 373 (13) [M^+–4CO], 188 (10), 170 (17), 118 (16), 105 (100), 77 (58) [$C_6H_6^+$], 42 (61), 28 (10) [CO^+]. Anal. Calc. for $C_{16}H_{15}NO_5W$ (485.2) C, 39.61; H, 3.12; N 2.89. Found: C, 39.52; H, 3.07; N, 2.93%.

4.4. Synthesis of $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_3$ (M = Cr: **5**; W: **6**) – general procedure

A solution of $(OC)_4M{=}C(\eta^2$-$NMeCH_2CH{=}CHCH_2OH)Me$ (M = Cr: **3a**, W: **4a**) (0.5 mmol) in THF (20 ml) was treated at −78 °C with ^{n}BuLi (0.31 ml of a 1.6 M solution in diethyl ether; 0.5 mmol). After 20 min Me_3SiCl (65 μl, 0.51 mmol) was added and the mixture was stirred at −78 °C for 30 min. The dark yellow solution was allowed to warm to room temperature, the solvent was removed in vacuo and the residue was taken up in diethyl ether (30 ml). The resulting solution was filtered to remove insoluble LiCl. The filtrate thus obtained was evacuated and the remaining solid was washed with pentane and dried in vacuo to give **5** or **6** as a yellow powder.

4.4.1. $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_3$ (**5**)

Yield: 153 mg (84%). m.p. 78 °C (dec.), $C_{14}H_{21}CrNO_5Si$. ^1H NMR (300 MHz): $\delta = 0.13$ (s, 9H, H^{SiMe}), 2.40 (s, 3H, H^{Me}), 3.25 (s, 3H, H^{NMe}), 3.68 (m, 1H, H^{NCH_2}), 4.00 (m, 1H, H^{CH}), 4.35 (m, 1H, H^{CH_2O}), 4.39 (m, 1H, H^{NCH_2}), 4.52 (m, 1H, H^{CH_2O}), 4.67 (m, 1H, H^{CH}). IR (ATR): $\nu = 2002/1887/1845$/cm^{-1} [ν(Cr(CO)$_4$)], 1549 [ν(C=C)]. EI-MS: m/z (%) = 363 (5) [M^+], 335 (1) [M^+–CO], 307 (3) [M^+–2CO], 279 (1) [M^+–3CO], 251 (15) [M^+–4CO], 182 (19), 141 (10), 126 (25), 110 (100), 73 (21) [$SiMe_3^+$], 52 (20) [Cr^+], 42 (9). Anal. Calc. for $C_{14}H_{21}CrNO_5Si$ (363.4) C, 46.27; H, 5.82; N 3.85. Found: C, 46.41; H, 5.77; N, 3.73%.

4.4.2. $(OC)_4W{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_3$ (**6**)

Yield: 223 mg (90%); m.p. 95 °C (dec.), $C_{14}H_{21}NO_5SiW$. ^1H NMR (250 MHz): $\delta = 0.14$ (s, 9H, H^{SiMe}), 2.54 (s, 3H, H^{Me}), 3.29 (s, 3H, H^{NMe}), 3.99 (m, 1H, H^{NCH_2}), 4.26 (m, 1H, H^{CH}), 4.38 (m, 1H, H^{CH_2O}), 4.46 (m, 1H, H^{NCH_2}), 4.73 (m, 1H, H^{CH_2O}), 4.80 (m, 1H, H^{CH}). IR (ATR): $\nu = 2016/1965/1886/1850$ cm^{-1} [ν(W(CO)$_4$)], 1541 [ν(C=C)]. EI-MS: m/z (%) = 495 (17) [M^+], 467 (2) [M^+–CO], 411 (14) [M^+–3CO], 383 (76) [M^+–4CO], 350 (56), 338 (29), 325 (20), 308 (17), 263 (10), 294 (10), 108 (9), 73 (100) [$SiMe_3^+$], 45 (45). Anal. Calc. for $C_{14}H_{21}NO_5SiW$ (495.3) C, 33.95; H, 4.27; N 2.83. Found: C, 34.04; H, 4.27; N, 2.91%.

4.5. Synthesis of $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_2SiMe_3$ (M = Cr: **7**; W: **8**) – general procedure

A solution of **3a** or **4a** (0.8 mmol) in THF (50 ml) was treated at −78 °C with ^{n}BuLi (1.05 ml of a 1.6 M solution in diethyl ether; 1.68 mmol) whereupon the reaction mixture turned dark and a precipitation formed immediately. After 20 min, Me_3SiCl (0.21 ml, 1.68 mmol) was added and the mixture was stirred at −78 °C for 30 min to give a clear yellow (**3a**) or dark orange (**4a**) solution, which was finally warmed to room temperature. After evaporation of the solvent in vacuo the residue was extracted with diethyl ether (50 ml) and the extract filtered to remove inorganic salts. Upon evaporation of the now clear filtrate, bright or dark orange oils were obtained, washed repeatedly with pentane and dried in vacuo to leave a dark yellow (**7**) or dark orange (**8**) air-sensitive oil.

4.5.1. $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_2SiMe_3$ (7)

Yield: 300 mg (86%); $C_{17}H_{29}CrNO_5Si_2$. ^{1}H NMR (250 MHz): $\delta = 0.14$ (s, 9H, H^{SiMe}), 0.22 (s, 9H, H^{OSiMe}), 2.74 (d, 1H, $^2J = 10.4$ Hz, H^{CH_2}), 2.99 (d, 1H, $^2J = 10.4$ Hz, H^{CH_2}), 3.20 (s, 3H, H^{NMe}), 3.78 (m, 1H, H^{NCH_2}), 4.11 (m, 1H, H^{CH}), 4.24 (m, 1H, H^{CH_2O}), 4.38 (m, 1H, H^{NCH_2}), 4.46 (m, 1H, H^{CH_2O}), 4.62 (m, 1H, H^{CH}). IR (ATR): $\nu = 2006/1968/1888/1860$ cm^{-1} [ν(Cr(CO)$_4$)], 1542 [ν(C=C)], 1250 [ν(SiMe$_3$)]. EI-MS: m/z (%) = 435 (6) [M$^+$], 407 (1) [M$^+$–CO], 379 (3) [M$^+$–2CO], 363 (16) [M$^+$–SiMe$_3$], 351(2) [M$^+$–3CO], 323 (9) [M$^+$–4CO], 251 (18), 182 (38), 141 (7), 127 (45), 110 (100), 93 (5), 73 (39) [SiMe$_3^+$], 52 (39) [Cr$^+$]. Anal. Calc. for $C_{17}H_{29}CrNO_5Si_2$ (435.6) C, 46.87; H, 6.71; N 3.21. Found: C, 46.72; H, 6.77; N, 3.23%.

4.5.2. $(OC)_4W{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OSiMe_3)CH_2SiMe_3$ (8)

Yield: 359 mg (79%); $C_{17}H_{29}NO_5Si_2W$. ^{1}H NMR (250 MHz): $\delta = 0.14$ (s, 9H, H^{SiMe}), 0.23 (s, 9H, H^{OSiMe}), 2.94 (d, 1H, $^2J = 10.3$ Hz, H^{CH_2}), 3.17 (d, 1H, $^2J = 10.3$ Hz, H^{CH_2}), 3.26 (s, 3H, H^{NMe}), 4.08 (m, 1H, H^{NCH_2}), 4.24 (m, 1H, H^{CH}), 4.43 (m, 1H, H^{CH_2O}), 4.48 (m, 1H, H^{NCH_2}), 4.75 (m, 1H, H^{CH_2O}), 4.81 (m, 1H, H^{CH}). IR (ATR): $\nu = 2015/1975/1853$ cm^{-1} [ν(W(CO)$_4$)], 1516 [ν(C=C)], 1249 [ν(SiMe$_3$)]. EI-MS: m/z (%) = 567 (6) [M$^+$], 539 (1) [M$^+$–CO], 483 (3) [M$^+$–3CO], 455 (10) [M$^+$–4CO], 381 (6), 73 (100) [SiMe$_3^+$], 45 (37). Anal. Calc. for $C_{17}H_{29}NO_5Si_2W$ (567.4) C, 35.98; H, 5.15; N 2.47. Found: C, 36.12; H, 5.17; N, 2.43%.

*4.6. Synthesis of $(OC)_4M{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)CH_2SiMe_3$ (M = Cr: **9**; W: **10**) – general procedure*

A solution of **7** or **8** (0.5 mmol) in diethyl ether (40 ml) was cooled to −78 °C and treated with water (20 ml). The reaction mixture was allowed to slowly warm up to room temperature and was then stirred for a further 30 min. The organic phase was separated, dried with $MgSO_4$ and concentrated in vacuo. The resulting residue was washed with pentane and dried on an oil pump to give **9** as a yellow and **10** as rufous powder.

4.6.1. $(OC)_4Cr{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)\ CH_2SiMe_3$ (9)

Yield: 173 mg (95%); m.p. 72 °C (dec.), $C_{14}H_{21}CrNO_5Si$. ^{1}H NMR (300 MHz): $\delta = 0.23$ (s, 9H, H^{SiMe}), 2.75 (d, 1H, $^2J = 10.4$ Hz, H^{CH_2}), 2.99 (d, 1H, $^2J = 10.4$ Hz, H^{CH_2}), 3.22 (s, 3H, H^{NMe}), 3.67 (m, 1H, H^{NCH_2}), 4.17 (m, 1H, H^{CH}), 4.32 (m, 1H, H^{CH_2OH}), 4.35 (br, 1H, H^{OH}), 4.37 (m, 1H, H^{NCH_2}), 4.46 (m, 1H, H^{CH_2OH}), 4.67 (m, 1H, H^{CH}). IR (ATR): $\nu = 3267$ cm^{-1} [ν(OH)], 2001/1943/1886/1840 [ν(Cr(CO)$_4$)], 1529 [ν(C=C)], 1250 [ν(SiMe$_3$)]. EI-MS: m/z (%) = 363 (8) [M$^+$], 347 (9) [M$^+$–Me], 323 (13), 307 (2) [M$^+$–2CO], 279 (3) [M$^+$–3CO], 251 (17) [M$^+$–4CO], 199 (17), 182 (100), 154 (22), 128 (20), 110 (23), 73 (69) [SiMe$_3^+$], 52 (55) [Cr$^+$]. Anal. Calc. for $C_{14}H_{21}CrNO_5Si$ (363.4) C, 46.27; H, 5.82; N 3.85. Found: C, 46.32; H, 5.87; N, 3.76%.

4.6.2. $(OC)_4W{=}C(\eta^2\text{-}NMeCH_2CH{=}CHCH_2OH)CH_2SiMe_3$ (10)

Yield: 252 mg (89%); m.p. 79 °C (dec.), $C_{14}H_{21}NO_5SiW$. ^{1}H NMR (250 MHz): $\delta = 0.22$ (s, 9H, H^{SiMe}), 2.93 (d, 1H, $^2J = 10.3$ Hz, H^{CH_2}), 3.15 (d, 1H, $^2J = 10.3$ Hz, H^{CH_2}), 3.24 (s, 3H, H^{NMe}), 3.93 (m, 1H, H^{NCH_2}), 4.04 (m, 1H, H^{CH}), 4.29 (br, 1H, H^{OH}), 4.31 (m, 1H, H^{CH_2OH}), 4.40 (m, 1H, H^{NCH_2}), 4.76 (m, 1H, H^{CH_2OH}), 4.94 (m, 1H, H^{CH}). IR (ATR): $\nu = 3372$ cm^{-1} [ν(OH)], 2015/1979/1848 [ν(W(CO)$_4$)], 1517 [ν(C=C)], 1250 [ν(SiMe$_3$)]. EI-MS: m/z (%) = 495 (2) [M$^+$], 467 (21) [M$^+$–CO], 439 (1) [M$^+$–2CO], 423 (2) [M$^+$–SiMe$_3$], 411 (1) [M$^+$–3CO], 268 (5), 212 (5), 184 (6), 147 (100), 116 (11), 73 (61) [SiMe$_3^+$]. Anal. Calc. for $C_{14}H_{21}NO_5SiW$ (495.3) C, 33.95; H, 4.27; N 2.83. Found: C, 34.11; H, 4.36; N, 2.77%.

Acknowledgements

We are grateful to Bayer and BASF for donations of chemicals.

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