

Syntheses, structures and electrochemistry of some 1-(η^2 -allylamino)-1-ferrocenylcarbene complexes of chromium(0), molybdenum(0) and tungsten(0) [☆]

Part 13: The chemistry of metallacyclic alkenylcarbene complexes

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Abstract

The metallacyclic complexes $(OC)_4M=C(\eta^2-NHCH_2CH=CHX)Fc$ (**4**; X = H) and (**5**; X = CH₂OH) [M = Cr: **a**; Mo: **b**; W: **c**; Fc = ferrocenyl = CpFe(C₅H₄)] were obtained in good yields upon photo-decarbonylation of the bimetallic allylaminocarbene complexes $(OC)_5M=C(NHCH_2CH=CHX)Fc$ (**2**; X = H)/(**3**; X = CH₂OH). At room temperature complexes **2/3** exist as mixtures of *E*- and predominantly *Z*-isomers with regard to the C–N bond. The molecular structures of **4b** and **4c** were determined by X-ray diffraction analyses. The intermetallic communicative effects and the interplay of Fc and η^2 -alkene moieties of **4a** and **4b** were assessed by cyclo-voltammetry. All complexes were also characterized in solution by one- and two-dimensional NMR spectroscopy (¹H, ¹³C, ¹H NOE, ¹H/¹H COSY, ¹³C/¹H HETCOR).

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1. Introduction

Stable metallacyclic (η^2 -alkene)carbene complexes of group VI transition metals [2–6] are ideal model systems for studying the elementary steps in olefin cyclopropanation [7–10] and metathesis [11–14]. This has been done at length by varying the central metal, the ancillary ligands and the alkene residues, as well as the spatial orientation of the η^2 -bonded ligands by adjusting the tether length. In contrast, the exometallacyclic residue on the carbene carbon atom has received little attention as a potential handle on the overall complex reactivity. We expected a ferrocenyl ligand [15] at the carbene carbon atom of (η^2 -alkene)carbene complexes to significantly increase their

stability and modify their reactivity. Early hints in this direction were reports by Dötz et al. [16] on the reaction of 1-methoxy-1-ferrocenyl-pentacarbonylchromium(0) [17] with tolan to give unexpected furanoid products, untypical of the Dötz benzannulation process. Similar reactions were found for the Mo and W congeners [18].

Rudler et al. [19] very recently reported that 1-ferrocenyl substituted chelated η^2 -allylaminocarbene complexes of Cr and Mo but not W can be prepared by a thermally induced alkene coordination of the corresponding allylaminocarbene complexes and also communicated the X-ray structures of the chromium series. Herein we report the synthesis of these and various other 1-ferrocenyl substituted chelated (η^2 -alkene)aminocarbene complexes of Cr, Mo and W, including such with additional hydroxy groups adjacent to the alkene ligand, by an alternative photo-decarbonylation/alkene ligation of the corresponding allylaminocarbene complexes in analogy to a previously

[☆] For Part 12, see [1].

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established method [20,21]. We also took a closer look at the *Z/E* ratios of the uncoordinated precursor complexes which are crucial for the yield of the photo-chelation step. The first X-ray structural analyses of chelated 1-ferrocenyl- $(\eta^2\text{-alkene})$ aminocarbene complexes of Mo and W are presented together with a comparison of the electrochemical behaviour of chelated and unchelated allylaminocarbene complexes of chromium and molybdenum.

2. Results and discussion

2.1. Synthesis and isomeric ratios of 1-(allylamino)-1-ferrocenylcarbene complexes $(OC)_5M=C(NHCH_2CH=CHX)Fc$ (**2**; $X = H$) and (**3**; $X = CH_2OH$)

Complexes of types **2** and **3** were prepared by aminolysis at room temperature of the respective 1-methoxy-1-ferrocenylcarbene complexes $(OC)_5M=C(OMe)Fc$ (**1**) ($M = Cr$: **1a**; Mo : **1b**; W : **1c**) with either a 10-fold excess of allylamine in Et_2O or a 4-fold excess of 1-aminobut-(2*Z*)-en-4-ol in THF, respectively, as described previously for similar 1-alkyl-1-allylaminocarbene complexes by us [21] and for the same 1-ferrocenyl-1-allylaminocarbene complexes **2a–c** very recently by the Rudler group [19] (Scheme 1). The required starting complexes **1** were obtained, according to a modified procedure by Connor and Lloyd [17], from the appropriate metal hexacarbonyls $M(CO)_6$, monolithioferrocene, and Meerwein salt $Me_3O^+BF_4^-$ in ca. 60–70% yield. The product complexes **2/3** were purified and the excess of amine was removed by column chromatography on silica gel 60. They were eluted as first fraction in each case with CH_2Cl_2 /hexane 1:2 (for **2**) or with neat diethyl ether (for **3**) and formed orange (**2a**) or bright red (**2b**, **2c**, **3**) air-sensitive powders upon drying. As only the *Z*-isomers of **2/3** are amenable to a photo-induced alkene ligation and as Rudler et al. [19] did not comment on the *Z/E* ratio of isomers of the complexes **2** which they obtained by Fischer aminolysis of the congenerous 1-ethoxy-1-ferrocenylcarbene complexes, we ascertained these ratios by NOE experiments. At room temperature complexes **2** and **3** actually exist as mixtures of *Z*- and *E*-isomers with regard

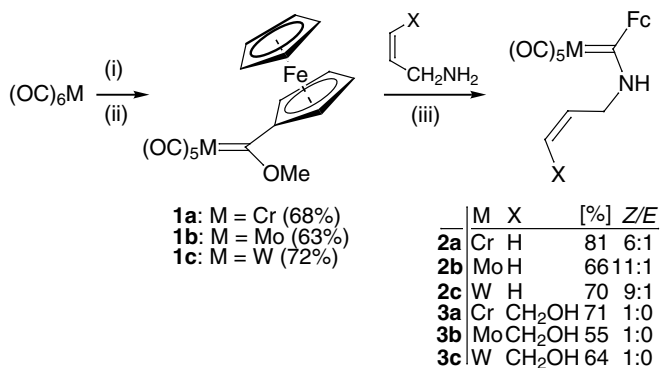
to the partial C–N double bond. Interestingly, and contrary to the analogous 1-alkyl or 1-aryl substituted aminocarbene complexes [21], the *Z*-isomers prevail by far with ratios ranging from 6:1 to 11:1 for complexes **2** and with the *E*-isomer of **3** not being detectable at all. This is presumably due to the bulkiness of the Fc residue. Such a pre-orientation of the side-chain is advantageous to the subsequent, photochemically induced chelation step. Also worthy of note is the fact that we have never observed the formation of the chelated molybdenum complex **4b** alongside that of the non-coordinated precursor **2b** as was reported by the Rudler group [19] for virtually identical reaction conditions.

Table 1 summarizes the ^{13}C NMR data of the individual isomers of **2** and **3**, while 1H NMR and other analytical data not reported in the literature are detailed in Section 3.

2.2. Photochemical synthesis and structures of chelated 1-(η^2 -allylamino)-1-ferrocenylcarbene complexes $(OC)_4M=C[(4,5-\eta^2)\text{-}NHCH_2CH=CHX]Fc$ (**4**; $X = H$) and (**5**; $X = CH_2OH$)

Irradiation of the complexes **2/3** at $-20^\circ C$ in THF led to the loss of a CO ligand and ligation of the alkene in the side-chain to give complexes **4a–c** and **5a–c**, respectively (Scheme 2). Whereas complexes **4a** and **4b** have been previously prepared by Rudler et al. [19] under thermal conditions (i.e., benzene, reflux, overnight), the tungsten complex **4c** could not be obtained by this method. Complexes **4** and **5** were generally purified by column chromatography on silica gel 60 under an atmosphere of dry argon. Complexes **4** were eluted as a dark red (second) band with a mixture of CH_2Cl_2 /hexane (1:2) while complexes **5** were eluted with diethyl ether. Evaporation and drying in high vacuum of the individual eluates left red air-sensitive powdery solids in yields ranging from ca. 60% to 75%. Crystalline batches suitable for single-crystal X-ray diffraction structural analyses were obtained of **4b** and **4c** by slow recrystallization from diethyl ether/hexane. To the best of our knowledge, no X-ray structure analysis of a chelated (η^2 -alkene)molybdenumcarbene complex has been published, so far. Table 2 lists the ^{13}C NMR data of the new complexes **4c** and **5**.

Fig. 1 depicts the molecular structures of complexes **4b** and **4c** as obtained from single-crystal X-ray diffraction analyses. As anticipated, they bear a high degree of structural similarity with almost identical bond lengths $d(M=C)$ and $d(C=C)$. More revealing, regarding the influence of the 1-ferrocenyl substituent, is a comparison of **4b** and **4c** with Casey's [3b] congenerous 1-*p*-tolyl tungsten complex **6** and Rudler's chromium analogues **4a** [19] and **7** [2c] (Fig. 2). While the C=C bond lengths are virtually the same for all five complexes, the W=C bond length of the tolyl substituted complex **6** (2.40 Å) is significantly larger than that (2.21 Å) of the 1-ferrocenyl complex **4c**, a fact which might be ascribed to a stronger electron-donating effect of the *p*-tolyl residue. The Cr=C bond length, which is 2.07 Å in both complexes



Scheme 1. Reagents and conditions: (i) LiFc, Et_2O , r.t., 6 h; (ii) $Me_3O^+BF_4^-$, CH_2Cl_2 , r.t., 18 h; (iii) for **2**: 10-fold excess of amine, Et_2O , r.t., 4 h; for **3**: 4-fold excess of amine, Et_2O/THF (5:1), r.t., 5 h.

Table 1
 ^{13}C NMR data^{a,b} of complexes (*Z/E*)-**2**^c and **Z-3**

| | $\delta^{13}\text{C}(\text{M}=\text{C})$ | $\delta^{13}\text{C}(-\text{CH}=\text{C})$ | $\delta^{13}\text{C}(\text{C}=\text{CH}_2)$ | $\delta^{13}\text{C}(-\text{CH}_2-)$ | $\delta^{13}\text{C}(\text{Fc})$ | $\delta^{13}\text{C}(\text{CO})$ |
|-------------|--|--|---|--|--|--|
| Z-2a | 266.4 (s) | 134.1 (s) | 118.8 (s) | 56.5 (s) | 70.6 (s, C ^{Cp}) 70.8 (s, C ^{2,5-Fc}) 72.0 (s, C ^{3,4-Fc}) 94.8 (s, C ^{1-Fc}) | 219 (s, C ^{eq}) 224.4 (s, C ^{ax}) |
| E-2a | 269.3 (s) | 134.4 (s) | 116.8 (s) | 54.5 (s) | 68.5 (s, C ^{Cp}) 72.9 (s, C ^{2,5-Fc}) 74.7 (s, C ^{3,4-Fc}) 86.9 (s, C ^{1-Fc}) | 219.3 (s, C ^{eq}) 224.1 (s, C ^{ax}) |
| Z-2b | 257.8 (s) | 134.3 (s) | 118.4 (s) | 58.0 (s) | 70.7 (s, C ^{Cp}) 71.6 (s, C ^{2,5-Fc}) 72.6 (s, C ^{3,4-Fc}) 92.5 (s, C ^{1-Fc}) | 207.9 (s, C ^{eq}) 214 (s, C ^{ax}) |
| E-2b | 261.2 (s) | 134.2 (s) | 116.9 (s) | 56.5 (s) | 70.6 (s, C ^{Cp}) 73.2 (s, C ^{2,5-Fc}) 76.0 (s, C ^{3,4-Fc}) 86.3 (s, C ^{1-Fc}) | 208.2 (s, C ^{eq}) 214.5 (s, C ^{ax}) |
| Z-2c | 246.9 (s) [90.4] | 134.0 (s) | 118.6 (s) | 58.8 (s) | 70.8 (s, C ^{Cp}) 72.1 (s, C ^{2,5-Fc}) 72.7 (s, C ^{3,4-Fc}) 93.7 (s, C ^{1-Fc}) | 199.6 (s, C ^{eq}) [126.4] 203.6 (s, C ^{ax}) [126.4] |
| E-2c | 249.5 (s) [93.6] | 129.7 (s) | 117.0 (s) | 54.6 (s) | 70.7 (s, C ^{Cp}) 73.3 (s, C ^{2,5-Fc}) 76.3 (s, C ^{3,4-Fc}) 87.5 (s, C ^{1-Fc}) | 200.6 (s, C ^{eq}) [127.6] 203.9 (s, C ^{ax}) [n.o.] |
| Z-3a | 264.1 (s) | 125.9 (s) 135.8 (s) | – | 51.6 (s, C ^{NCH2}) 59.1 (s, C ^{CH2O}) | 70.6 (s, C ^{Cp}) 70.7 (s, C ^{2,5-Fc}) 71.9 (s, C ^{3,4-Fc}) 94.8 (s, C ^{1-Fc}) | 219.1 (s, C ^{eq}) 224.4 (s, C ^{ax}) |
| Z-3b | 256.1 (s) | 126.1 (s) 135.6 (s) | – | 53.4 (s, C ^{NCH2}) 59.2 (s, C ^{CH2O}) | 70.8 (s, C ^{Cp}) 71.7 (s, C ^{2,5-Fc}) 72.6 (s, C ^{3,4-Fc}) 92.8 (s, C ^{1-Fc}) | 208.1 (s, C ^{eq}) 214.4 (s, C ^{ax}) |
| Z-3c | 245.1 (s) [90.0] | 125.9 (s) 135.6 (s) | – | 54.1 (s, C ^{NCH2}) 59.2 (s, C ^{CH2O}) | 70.8 (s, C ^{Cp}) 72.1 (s, C ^{2,5-Fc}) 72.6 (s, C ^{3,4-Fc}) 93.9 (s, C ^{1-Fc}) | 199.8 (s, C ^{eq}) [126.3] 203.8 (s, C ^{ax}) [126.6] |

^a Solutions in acetone-*d*₆ (saturated; at 23 °C).

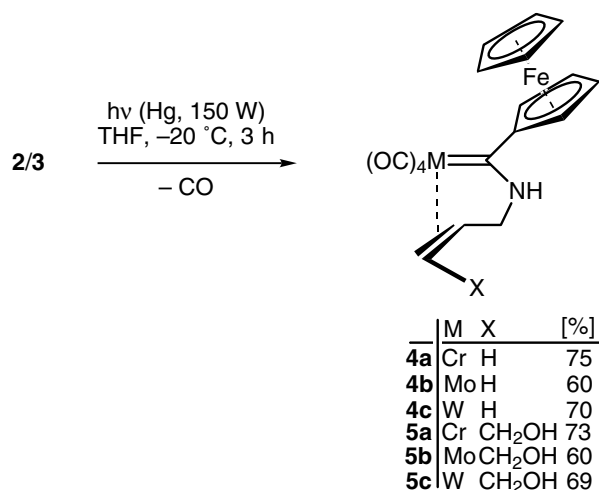
^b Coupling constants $^nJ(^{183}\text{W}, ^{13}\text{C})$ are given in parentheses (± 0.1 Hz).

^c **2a**: *Z/E* \approx 6:1, **2b**: *Z/E* \approx 11:1, **2c**: *Z/E* \approx 9:1.

4a and **7**, seems to be less susceptible to the influence of the 1-substituent. The overall spatial orientation of the alkene–carbene chelate ligand is conspicuously similar in the complexes **4**, **6**, and **7** and hardly dependent on the nature of the central metal or the *exo*-metallacyclic substituent at the carbene carbon atom.

This fact is reflected by a neglectable variance of the descriptive angles α , β , and γ as defined by Casey [3b] (Fig. 2). α is the angle between the olefin midpoint, the metal and the carbene carbon atom. β is the dihedral angle

between the plane containing the carbene carbon, the metal and the olefin midpoint and the plane defined by the metal and the two alkene C-atoms. β is 0° for parallel [M=C] and [C=C] units and it is 90° for a perpendicular arrangement of these groups. The closer to 0° β is, the more prone these complexes are to intramolecular cyclopropanation or metathesis reactions. The angle γ is independent of olefin rotation and describes the twist between the plane of the carbene carbon, the metal, and the alkene midpoint and the plane of the carbene moiety [CR¹(NR²)]. Obviously,



Scheme 2.

the complexes **4–7** draw a good deal of stability from geometrical constraints imposed by the small 5.5-membered metallacycle that prevent a collinear orientation of the C=C and M=C bonds and cause a considerable tilt of the “carbene plane” [CR¹(NR²)] with respect to the olefin (i.e., a small angle γ).

2.3. Cyclic voltammetry of complexes (OC)₄M=C[(4,5- η^2)-NHCH₂CH=CH₂]Fc (**4**)

For the identification of potential communicative effects between the two metal centres in complexes **4**, cyclic voltammograms [22] were recorded of **4a** and **4b** in acetonitrile solutions against an Ag/AgNO₃ reference electrode and with optionally added ferrocene as an internal calibrant (Fig. 3). Solutions of **4c** decomposed too quickly and gave ill-resolved CVs. Non-chelated α -ferrocenyl substituted pentacarbonylaminocarbene complexes of chromium and tungsten were reported in the literature [22a] to give but a single one-electron oxidation wave in the CVs, despite their containing two individual redox-active moieties A and B [i.e., Fc and (OC)₅M=C]. This was rationalized by assuming that the redox orbital of (OC)₅MC(X)Fc would encompass both redox centres corresponding to the generation of a “mixed” species [A–B]⁺. However, when the CV of complex **4a** was recorded by commencing the sweeps at –250 mV and going initially to positive potentials (oxidative direction), four distinct redox steps of which the first three were reversible one-electron processes cropped up. It is tempting, though arbitrary, to assign the first one at $E_{1/2} = 1/2(E_{pa} + E_{pc}) = -100$ mV vs. Ag/AgNO₃ with $\Delta E_p = 80$ mV to the

Table 2
¹³C NMR data^{a,b} of new complexes **4c** and **5**

| | δ ¹³ C(M=C) | δ ¹³ C(–CH=) | δ ¹³ C(=CH ₂) | δ ¹³ C(–CH ₂ –) | δ ¹³ C(Fc) | δ ¹³ C(CO) |
|-----------|-------------------------------|--|---|--|---|--|
| 4c | 253.0 (s) [86.0] | 74.3 (s) [7.4] | 58.3 (s) [6.4] | 53.8 (s) | 68.4 (s, C ^{2,5-Fc}) 70.6 (s, C ^{Cp}) 73.1 (s, C ^{3,4-Fc}) 73.5 (s, C ^{3,4-Fc}) 74.8 (s, C ^{2,5-Fc}) 88.1 (s, C ^{1-Fc}) [7.7] | 206.0 (s) [120.1] 206.7 (s) [122.0] 210.4 (s) [135.9] 217.6 (s) [154.2] |
| 5a | 269.0 (s) | 78.7 (s) 87.2 (s) | – | 51.0 (s, C ^{NCH₂}) 62.2 (s, C ^{CH₂O}) | 66.9 (s, C ^{2,5-Fc}) 70.5 (s, C ^{Cp}) 72.6 (s, C ^{3,4-Fc}) 73.1 (s, C ^{3,4-Fc}) 74.4 (s, C ^{2,5-Fc}) 87.5 (s, C ^{1-Fc}) | 226.1 (s) 226.7 (s) 227.8 (s) 235.8 (s) |
| 5b | 261.9 (s) | 86.4 (s) 95.0 (s) | – | 51.0 (s, C ^{NCH₂}) 61.6 (s, C ^{CH₂O}) | 69.8 (s, C ^{2,5-Fc}) 70.7 (s, C ^{Cp}) 73.1 (s, C ^{3,4-Fc}) 73.19 (s, C ^{3,4-Fc}) 73.22 (s, C ^{2,5-Fc}) 88.6 (s, C ^{1-Fc}) | 211.9 (s) 213.2 (s) 218.6 (s) 222.8 (s) |
| 5c | 250.6 (s) [86.0] | 71.0 (s) [4.6] 82.7 (s) [6.6] | – | 51.2 (s, C ^{NCH₂}) 62.6 (s, C ^{CH₂O}) | 68.6 (s, C ^{2,5-Fc}) 70.9 (s, C ^{Cp}) 73.0 (s, C ^{3,4-Fc}) 73.3 (s, C ^{3,4-Fc}) 74.9 (s, C ^{2,5-Fc}) 89.0 (s, C ^{1-Fc}) [7.8] | 205.0 (s) [118.7] 207.3 (s) [125.9] 210.0 (s) [134.8] 216.6 (s) [153.2] |

^a Solutions in acetone-*d*₆ (saturated; at 23 °C).

^b Coupling constants ⁿJ(¹⁸³W, ¹³C) are given in parentheses (±0.1 Hz).

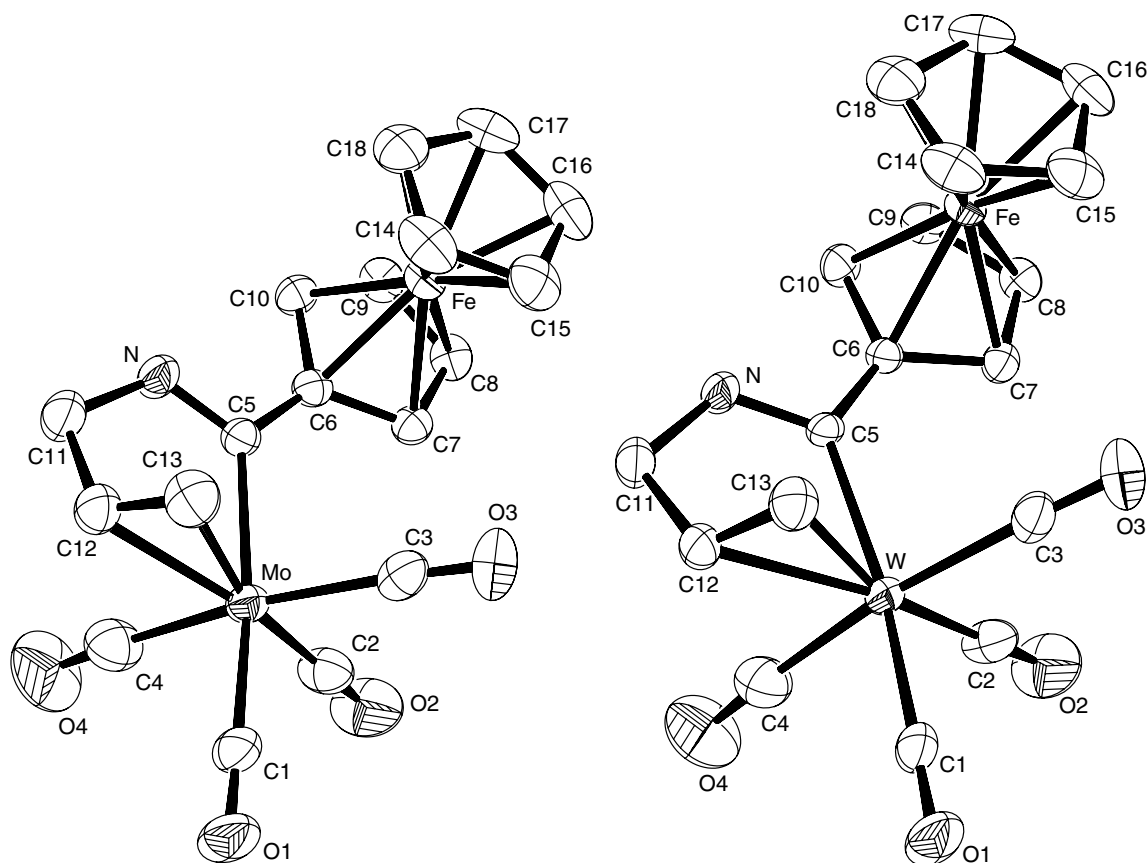


Fig. 1. Molecular structures of **4b** (left) and **4c** (right) (ORTEP representations, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°) of **4b**/**4c**: M–C5 2.226(3)/2.2072, M–C12 2.395(3)/2.3744, M–C13 2.417(3)/2.3975, M–C1 1.982(3)/1.9813, M–C2 1.992(4)/1.9917, M–C3 2.041(3)/2.0371, C5–C6 1.462(4)/1.4682, N–C5 1.309(4)/1.3093, N–C11 1.467(4)/1.4593, C11–C12 1.504(4)/1.5006, C12–C13 1.355(4)/1.3768; C12–M–C13 32.72(10)/33.53, M–C13–C12 72.75(16)/72.31, C11–C12–C13 121.8(3)/121.68, M–C5–N 115.56(19)/116.72, C5–M–C12 74.76(9)/74.18, N–C5–C6–Fe 79.1(3)/79.55, N–C5–C6–C10 9.8(4)/9.58, C11–N–C5–M 6.6(4)/6.26, N–C11–C12–C13 49.3(4)/49.92.

| | M | R ¹ | R ² | d _{M=C} | d _{C=C} | α/° | β/° | γ/° |
|-----------|----|-----------------|----------------|------------------|------------------|-----|-----|-----|
| 4a | Cr | Fc | H | 2.07 | 1.36 | 80 | 81 | 28 |
| 4b | Mo | Fc | H | 2.22 | 1.35 | 77 | 80 | 26 |
| 4c | W | Fc | H | 2.21 | 1.37 | 77 | 79 | 27 |
| 6 | W | <i>p</i> -Tolyl | H | 2.40 | 1.38 | 77 | 77 | 26 |
| 7 | Cr | Me | Me | 2.07 | 1.36 | – | 90 | 27 |

Fig. 2. Structural comparison of (η^2 -allylamino)carbene complexes **4**, **6** [**3b**] and **7** [**2c**]. Bond lengths $d(\text{M}=\text{C})$ and $d(\text{C}=\text{C})$ given in Å; descriptive angles α , β , γ as defined by Casey [**3b**].

Fe(II)/Fe(III) couple of the 1-ferrocenyl ligand, as free ferrocene gives a reversible wave close by at $E_{1/2} = -80$ mV with $\Delta E_p = 60$ mV. The following reversible waves of **4a** were centred at $E_{1/2} = 100$ mV and $E_{1/2} = 280$ mV both with $\Delta E_p = 60$ mV. A final peak around 820 mV belonged to an irreversible oxidation. Interestingly, the CV curve of the congenerous 1-methyl substituted complex $(\text{OC})_4\text{Cr}=\text{C}[(4,5-\eta^2)\text{-NHCH}_2\text{CH}=\text{CH}_2]\text{Me}$ (**8**) also featured three oxidation steps (at -60 , 270, ca. 800 mV), all shifted towards more negative potentials when compared to those of **4a** and all less pronounced and flatter. Only the second one showed signs of

reversibility with a reductive peak around 190 mV ($\Delta E_p = 80$ mV). This also disagrees with the literature which reports a drop (i.e., cathodic shift) in the oxidation potentials upon replacement of alkyl or aryl substituents with Fc in various chromium or tungsten pentacarbonyl-carbene complexes [**22a**]. By contrast with **4a** but in line with the literature on non-chelated complexes $(\text{OC})_5\text{-MC(X)Fc}$ (M = Cr, W), the voltammogram of molybdenum complex **4b** had only one clear-cut reversible redox couple at $E_{1/2} = 90$ mV with $\Delta E_p = 60$ mV. To acquire some idea of the energetic spacing of the redox-pertinent frontier orbitals and their spatial distribution and coefficients, we performed hybrid density functional (B3LYP) single point calculations [**23**] for **4a** and **4b** using the geometry obtained from the X-ray structure analyses. The four frontmost occupied MOs were calculated very similar pairwise for **4a** and **4b** as to the spatial shape and coefficients. The upper three MOs are mainly localized about the $(\text{OC})_4\text{M}$ moiety, the HOMO – 3 on the Fc residue. These four topmost MOs were in either case very tightly spaced in terms of energy, but markedly more so for the molybdenum complex **4b**, spanning a range of merely 0.03 eV for **4b**, but 0.05 eV for **4a**. These

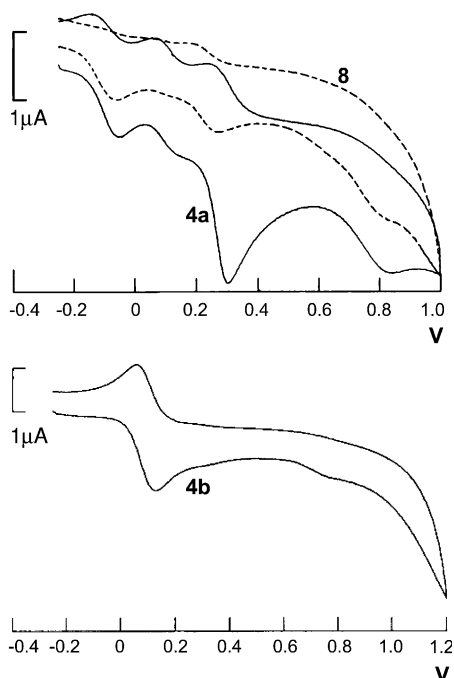


Fig. 3. Cyclovoltammograms of **4a** (top), **8** (top, dashed) and **4b** (bottom), each as 10^{-4} M solution in MeCN/ Bu_4NClO_4 (0.1 M), r.t., at Pt vs. Ag/AgNO₃, sweep rate 200 mV/s, scan range $-250 < E < 1000/1200$ mV.

computational results could help explain the differences in the cyclovoltammograms and also warn against interpreting individual redox steps as originating solely from a particular isolated redox subsystem such as the ferrocenyl or the $(\text{OC})_4\text{M}$ portion.

2.4. Conclusion

We have prepared and characterized various 1-ferrocenyl substituted chelated and non-chelated alkene–carbene complexes of chromium, tungsten and molybdenum. Generally, ligation of the olefinic C=C bond seems to diminish, or partly compensate for the donor effect of the 1-Fc substituent thus maintaining the carbene function relatively electrophilic and the whole complex less prone to oxidation than the congenerous 1-Fc carbene complexes with uncoordinated side-arm alkenes or with ordinary 1-alkyl or 1-aryl substituents. This is reflected in the X-ray geometries and the cyclovoltammograms. Complexes **4a** and **4c** showed a low reactivity towards alkynes such as diphenylacetylene and 3-hexyne which fact can be rationalized by sterical hindrance and the reluctance of the alkene ligand to give way to the alkyne. Once initiated under forcing conditions the reactions with alkynes proceeded unspecifically yielding various decomposition products rather than furans or cyclobutenones. Further work is currently underway in order to exploit the modulatory effect of the η^2 -alkene–1-Fc couple.

3. Experimental

3.1. General information

Preparation and handling of all compounds was carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. The starting materials $\text{M}(\text{CO})_6$ (M = Cr, Mo, W), $(\text{C}_5\text{H}_5)_2\text{Fe}$, $\text{Me}_3\text{O}^+\text{BF}_4^-$, and $\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$ were purchased from Aldrich and used without further purification. Monolithioferrocene, LiFc, was prepared according to the literature procedure by Kagan et al. [24a]. For an alternative method see [24b].

NMR spectroscopy: Bruker ARX 250 and DRX 300 (^1H , ^{13}C); chemical shifts given with respect to Me_4Si [δ ^1H (CDCl_3) = 7.24, ($\text{CD}_3\text{COCD}_2\text{H}$) = 2.04; δ ^{13}C (CDCl_3) = 77.0, (CD_3COCD_3) = 29.8, 204.0]. IR spectra: Perkin–Elmer, Spectrum One FT-IR spectrophotometer equipped with an ATR sampling unit. EI-MS: Finnigan MAT 8500 (ionization energy 70 eV). Elemental analysis: Heraeus Mikromat C–H–N. Cyclovoltammetry: Princeton Appl. Research Potentiostat/Galvanostat Model 263 A operating M270 Research Electrochemistry software.

3.2. Synthesis of $(\text{OC})_5\text{M}=\text{C}(\text{OMe})\text{Fc}$ (**1**) – general procedure

Freshly prepared LiFc (1.92 g, 10.0 mmol) was dissolved in Et_2O (100 mL) at 0°C . 10 mmol of the respective metal hexacarbonyl $\text{M}(\text{CO})_6$ (M = Cr, Mo, W) was added in one portion and the resulting mixture was stirred for 5 h while slowly warming up to room temperature. The solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (100 mL) and treated with $\text{Me}_3\text{O}^+\text{BF}_4^-$ (1.48 g, 10.0 mmol). The mixture was stirred overnight, the solvent was removed in high vacuum and the remainder was chromatographed (silica gel 60; Et_2O). Evaporation of the eluates left deep purple, moderately air-sensitive powdery complexes **1**.

3.2.1. $(\text{OC})_5\text{Cr}=\text{C}(\text{OMe})\text{Fc}$ (**1a**)

M.p. 132°C (dec.) (lit. [17]: 134 – 135°C , dec.); Yield: 2.86 g (68%). ^1H NMR (300.13 MHz, CDCl_3): δ = 4.23 (s, 5H, H^{Cp}), 4.67 (m, 3H, H^{Me}), 4.78 (vt, 2H, $\text{H}^{3,4\text{-Fc}}$), 4.98 (vt, 2H, $\text{H}^{2,5\text{-Fc}}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 66.0 (OMe), 70.5, 72.2, 74.6, 93.6 (Fc), 217.3, 222.9 (CO), 333.0 (C-1). IR (ATR): 2051/1977/1946/1920/1888 cm^{-1} [$\nu(\text{Cr}(\text{CO})_5$)], 1429 [$\nu(\text{Cp})$]. EI-MS: m/z (%) = 420 (13) [M^+], 364 (13), 336 (16), 308 (18), 280 (82), 265 (7), 237 (100).

3.2.2. $(\text{OC})_5\text{Mo}=\text{C}(\text{OMe})\text{Fc}$ (**1b**)

M.p. 96°C (dec.); Yield: 2.92 g (63%). ^1H NMR (300.13 MHz, CDCl_3): δ = 4.24 (s, 5H, H^{Cp}), 4.57 (m, 3H, H^{Me}), 4.81 (vt, 2H, $\text{H}^{3,4\text{-Fc}}$), 4.97 (vt, 2H, $\text{H}^{2,5\text{-Fc}}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 67.9 (OMe), 70.6, 72.7, 75.0, 93.3 (Fc), 206.5, 212.7 (CO), 323.3 (C-1). IR (ATR): 2060/1980/1948/1920/1888 cm^{-1} [$\nu(\text{Mo}(\text{CO})_5$)], 1429 [$\nu(\text{Cp})$]. EI-MS: m/z (%) = 464 (49) [M^+], 433 (24),

380 (58), 352 (69), 324 (67), 283 (100). Anal. Calc. for $C_{17}H_{12}FeMoO_6$ (464.1): C, 44.00; H, 2.61. Found: C, 44.12; H, 2.68%.

3.2.3. $(OC)_5W=C(OMe)Fc$ (**1c**)

M.p. 120 °C (dec.); Yield: 3.97 g (72%). 1H NMR (300.13 MHz, $CDCl_3$): δ = 4.25 (s, 5H, H^{Cp}), 4.51 (m, 3H, H^{Me}), 4.83 (vt, 2H, $H^{3,4-Fc}$), 4.97 (vt, 2H, $H^{2,5-Fc}$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 68.6 (OMe), 70.8, 73.2, 75.1, 95.2 (Fc), 198.0, 202.3 (CO), 307.6 (C-1). IR (ATR): 2060/1975/1944/1915/1882 cm^{-1} [$\nu(W(CO)_5$)], 1429 [$\nu(Cp)$]. EI-MS: m/z (%) = 552 (72) [M^+], 496 (36), 468 (35), 440 (36), 425 (55), 412 (76), 369 (100). Anal. Calc. for $C_{17}H_{12}FeO_6W$ (552.0): C, 36.99; H, 2.19. Found: C, 37.10; H, 2.11%.

3.3. Synthesis of $(OC)_5M=C(NHCH_2CH=CH_2)Fc$ (**2**) – general procedure

Allylamine (1.14 g, 20.0 mmol) was dissolved in Et_2O (5 mL) and added at once to a solution of the respective complex **1** (2.0 mmol) in Et_2O (50 mL). The mixture was stirred at room temperature for 4 h. After removal of the solvent in vacuo, the remainder was chromatographed (silica gel 60; CH_2Cl_2 /hexane 1:2, v/v). The eluate (first fraction) was evaporated to leave **2** as an orange powder, which was dried on an oil pump.

3.3.1. $(Z/E)-(OC)_5Cr=C(NHCH_2CH=CH_2)Fc$ (**2a**) [19]

Mixture of *Z*- and *E*-isomers (*Z/E* \approx 6:1); Yield: 721 mg (81%), m.p. 80 °C (lit. [19]: no m.p. quoted). 1H NMR (300.13 MHz, acetone- d_6): *Z*-**2a**: δ = 4.26 (s, 5H, H^{Cp}), 4.59 (vt, 2H, $H^{3,4-Fc}$), 4.73 (m, 2H, H^{CH_2}), 4.88 (vt, 2H, $H^{2,5-Fc}$), 5.37 (dd, $^3J = 10.4$, $^2J = 1.5$ Hz, 1H, $H^{=CH_2}$), 5.44 (dd, $^3J = 17.3$, $^2J = 1.5$ Hz, 1H, $H^{=CH_2}$), 6.13 (ddt, $^3J = 17.3$, 10.4, 5.5 Hz, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}); *E*-**2a**: δ = 4.31 (s, 5H, H^{Cp}), 4.67 (vt, 2H, $H^{3,4-Fc}$), 4.74 (vt, 2H, $H^{2,5-Fc}$), 4.92 (m, 2H, H^{CH_2}), 5.30 (dd, $^3J = 10.6$, $^2J = 1.2$ Hz, 1H, $H^{=CH_2}$), 5.34 (dd, $^3J = 16.0$, $^2J = 1.2$ Hz, 1H, $H^{=CH_2}$), 6.11 (ddm, $^3J = 16.0$, 10.6 Hz, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}). IR (ATR): 3306 cm^{-1} [$\nu(NH)$], 2048/1979/1964/1891/1855 [$\nu(Cr(CO)_5$)], 1533 [$\nu(C=C)$], 1435 [$\nu(Cp)$]. EI-MS: m/z (%) = 445 (6) [M^+], 417 (7), 389 (3), 370 (20), 361 (13), 333 (28), 305 (36), 278 (100), 253 (42), 237 (42), 222 (83), 207 (21), 187 (12) [Fc^+]. Anal. Calc. for $C_{19}H_{15}Cr-FeNO_5$ (445.2): C, 51.26; H, 3.40; N, 3.15. Found: C, 51.31; H, 3.48; N, 3.14%.

3.3.2. $(Z/E)-(OC)_5Mo=C(NHCH_2CH=CH_2)Fc$ (**2b**) [19]

Mixture of *Z*- and *E*-isomers (*Z/E* \approx 11:1); Yield: 645 mg (66%), m.p. 85 °C (dec.) (lit. [19]: no m.p. quoted). 1H NMR (300.13 MHz, acetone- d_6): *Z*-**2b**: δ = 4.26 (s, 5H, H^{Cp}), 4.63 (vt, 2H, $H^{3,4-Fc}$), 4.68 (m, 2H, H^{CH_2}), 4.95 (vt, 2H, $H^{2,5-Fc}$), 5.34 (dd, $^3J = 10.4$, $^2J = 1.2$ Hz, 1H, $H^{=CH_2}$),

5.39 (dd, $^3J = 17.2$, $^2J = 1.2$ Hz, 1H, $H^{=CH_2}$), 6.12 (ddt, $^3J = 17.2$, 10.4, 5.5 Hz, 1H, H^{CH}), 9.9 (br, 1H, H^{NH}); *E*-**2b**: δ = 4.31 (s, 5H, H^{Cp}), 4.56 (vt, 2H, $H^{3,4-Fc}$), 4.75 (vt, 2H, $H^{2,5-Fc}$), 4.81 (m, 2H, H^{CH_2}), 5.31 (m, 1H, $H^{=CH_2}$), 5.35 (m, 1H, $H^{=CH_2}$), 6.14 (m, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}). IR (ATR): 3311 cm^{-1} [$\nu(NH)$], 2061/1986/1969/1885/1857 [$\nu(Mo(CO)_5$)], 1531 [$\nu(C=C)$], 1437 [$\nu(Cp)$]. EI-MS: m/z (%) = 489 (3) [M^+], 461 (4), 433 (2), 405 (3), 377 (17), 349 (31), 320 (15), 265 (14), 253 (100), 226 (33), 211 (20), 199 (36), 187 (21) [Fc^+]. Anal. Calc. for $C_{19}H_{15}Fe-MoNO_5$ (489.1): C, 46.66; H, 3.31; N, 2.86. Found: C, 46.53; H, 3.30; N, 2.80%.

3.3.3. $(Z/E)-(OC)_5W=C(NHCH_2CH=CH_2)Fc$ (**2c**) [19]

Mixture of *Z*- and *E*-isomers (*Z/E* \approx 9:1); Yield: 796 mg (69%), m.p. 110 °C (dec.) (lit. [19]: no m.p. quoted). 1H NMR (300.13 MHz, acetone- d_6): *Z*-**2c**: δ = 4.27 (s, 5H, H^{Cp}), 4.64 (m, 2H, H^{CH_2}), 4.65 (vt, 2H, $H^{3,4-Fc}$), 4.97 (vt, 2H, $H^{2,5-Fc}$), 5.35 (dd, $^3J = 10.4$, $^2J = 1.4$ Hz, 1H, $H^{=CH_2}$), 5.40 (dd, $^3J = 17.3$, $^2J = 1.4$ Hz, 1H, $H^{=CH_2}$), 6.13 (ddt, $^3J = 17.3$, 10.4, 5.5 Hz, 1H, H^{CH}), 9.9 (br, 1H, H^{NH}); *E*-**2c**: δ = 4.32 (s, 5H, H^{Cp}), 4.71 (vt, 2H, $H^{3,4-Fc}$), 4.79 (vt, 2H, $H^{2,5-Fc}$), 4.82 (m, 2H, H^{CH_2}), 5.29 (dd, $^3J = 10.4$, $^2J = 1.4$ Hz, 1H, $H^{=CH_2}$), 5.35 (dd, $^3J = 16.6$, $^2J = 1.4$ Hz, 1H, $H^{=CH_2}$), 6.16 (ddm, $^3J = 16.6$, 10.4 Hz, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}). IR (ATR): 3323 cm^{-1} [$\nu(NH)$], 2059/1966/1941/1868/1842 [$\nu(W(CO)_5$)], 1520 [$\nu(C=C)$], 1437 [$\nu(Cp)$]. EI-MS: m/z (%) = 577 (13) [M^+], 549 (9), 521 (1), 493 (13), 465 (27), 437 (100), 408 (36), 367 (42), 351 (31), 314 (24). Anal. Calc. for $C_{19}H_{15}Fe-NO_5W$ (577.0): C, 39.55; H, 2.62; N, 2.43. Found: C, 39.71; H, 2.71; N, 2.37%.

3.4. Synthesis of $(OC)_5M=C(NHCH_2CH=CHCH_2OH)Fc$ (**3**) – general procedure

1-Amino-but-(2*Z*)-en-4-ol (700 mg, 8.0 mmol) was dissolved in THF (10 mL) and added at once to a solution of the respective complex **1** (2.0 mmol) in Et_2O (50 mL). The mixture was stirred at room temperature for 5 h. After removal of the solvent in vacuo, the remainder was chromatographed (silica gel 60, Et_2O). The eluate (first fraction) was evaporated to leave the product complex **3** as an orange powder, which was dried on an oil pump.

3.4.1. $(1Z)-(OC)_5Cr=C(NHCH_2CH=CHCH_2OH)Fc$ (**3a**)

M.p. 86 °C (dec.); Yield: 674 mg (71%). 1H NMR (300.13 MHz, acetone- d_6): δ = 4.24 (s, 5H, H^{Cp}), 4.33 (br, 1H, H^{OH}), 4.37 (m, 2H, H^{NCH_2}), 4.55 (vt, 2H, $H^{3,4-Fc}$), 4.80 (m, 2H, H^{OCH_2}), 4.81 (vt, 2H, $H^{2,5-Fc}$), 5.85 (m, 1H, H^{CH}), 5.99 (m, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}). IR (ATR): 3438 cm^{-1} [$\nu(OH)$], 3287 [$\nu(NH)$], 2051/1964/1926/1897/1873 [$\nu(Cr(CO)_5$)], 1533 [$\nu(C=C)$], 1433 [$\nu(Cp)$]. EI-MS: m/z (%) = 475 (2) [M^+], 465 (8), 447 (1), 391 (1), 335 (2), 267 (32), 211 (66), 200 (97), 187 (44)

[Fc⁺], 121 (100), 56 (48) [Fe⁺]. Anal. Calc. for C₂₀H₁₇Cr-FeNO₆ (475.2): C, 50.55; H, 3.61; N, 2.95. Found: C, 39.71; H, 2.71; N, 2.86%.

3.4.2. (1Z)-(OC)₅Mo=C(NHCH₂CH=CHCH₂OH)Fc (3b)

M.p. 77 °C (dec.); Yield: 571 mg (55%). ¹H NMR (300.13 MHz, acetone-*d*₆): δ = 4.26 (s, 5H, H^{Cp}), 4.30 (br, 1H, H^{OH}), 4.36 (m, 2H, H^{NCH₂}), 4.62 (vt, 2H, H^{3,4-Fc}), 4.72 (m, 2H, H^{CH₂O}), 4.90 (vt, 2H, H^{2,5-Fc}), 5.79 (m, 1H, H^{CH}), 5.97 (m, 1H, H^{CH}), 9.9 (br, 1H, H^{NH}). IR (ATR): 3398 cm⁻¹ [ν(OH)], 3287 [ν(NH)], 2059/1984/1900/1875 [ν(Mo(CO)₅)], 1533 [ν(C=C)], 1431 [ν(Cp)]. EI-MS: *m/z* (%) = 519 (1) [M⁺], 463 (2), 377 (1), 370 (7), 361 (3), 263 (100), 198 (12), 187 (6) [Fc⁺]. Anal. Calc. for C₂₀H₁₇Fe-MoNO₆ (519.1): C, 46.27; H, 3.30; N, 2.70. Found: C, 46.17; H, 3.22; N, 2.76%.

3.4.3. (1Z)-(OC)₅W=C(NHCH₂CH=CHCH₂OH)Fc (3c)

M.p. 108 °C (dec.); Yield: 777 mg (64%). ¹H NMR (300.13 MHz, acetone-*d*₆): δ = 4.26 (s, 5H, H^{Cp}), 4.28 (br, 1H, H^{OH}), 4.37 (m, 2H, H^{NCH₂}), 4.55 (vt, 2H, H^{3,4-Fc}), 4.80 (m, 2H, H^{CH₂O}), 4.81 (vt, 2H, H^{2,5-Fc}), 5.85 (m, 1H, H^{CH}), 5.99 (m, 1H, H^{CH}), 10.1 (br, 1H, H^{NH}). IR (ATR): 3398 cm⁻¹ [ν(OH)], 3291 [ν(NH)], 2058/1977/1864 [ν(W(CO)₅)], 1533 [ν(C=C)], 1433 [ν(Cp)]. EI-MS: *m/z* (%) = 607 (1) [M⁺], 551 (1), 494 (2), 466 (3), 449 (7), 411 (10), 352 (30), 296 (23), 268 (57), 211 (53), 199 (52), 121 (100), 56 (67) [Fe⁺]. Anal. Calc. for C₂₀H₁₇FeNO₆W (607.1): C, 39.57; H, 2.82; N, 2.31. Found: C, 39.63; H, 2.82; N, 2.24%.

3.5. Synthesis of (OC)₄M=C[(4,5-η²)-NHCH₂CH=CHX]Fc (X = H: 4, X = CH₂OH: 5) – general procedure

A solution of complex **2** or **3**, respectively, (2.0 mmol) in THF (80 mL) was irradiated at –20 °C for 3 h with a Heraeus low-pressure mercury lamp (150 W) in an apparatus described elsewhere [20]. The solvent was removed in vacuo and the resulting residue was chromatographed on silica gel. The second red fraction eluted with a CH₂Cl₂/hexane (1:2) mixture in the case of **4**, or with neat Et₂O in the case of **5**, was collected and evaporated to dryness. The remaining red powdery products were dried in high vacuum.

3.5.1. (OC)₄Cr=C[(4,5-η²)-NHCH₂CH=CH₂]Fc (4a)

M.p. 122 °C (lit. [19]: no m.p. quoted); Yield: 609 mg (73%). ¹H NMR (300.13 MHz, acetone-*d*₆): δ = 3.08 (d, ³J = 13.3 Hz, 1H, H^{CH₂}), 3.18 (d, ³J = 9.1 Hz, 1H, H^{CH₂}), 4.13 (m, 1H, H^{=CH₂}), 4.25 (s, 5H, H^{Cp}), 4.28 (m, 1H, H^{=CH₂}), 4.55 (vt, 1H, H^{3,4-Fc}), 4.60 (vt, 1H, H^{3,4-Fc}), 4.76 (vt, 1H, H^{2,5-Fc}), 4.87 (m, 1H, H^{CH}), 4.89 (vt, 1H, H^{2,5-Fc}), 9.58 (br, 1H, H^{NH}). IR (ATR): 3328 cm⁻¹ [ν(NH)], 2004/1903/1891/1844/1831 [ν(Cr(CO)₄)], 1536 [ν(C=C)], 1438 [ν(Cp)]. EI-MS: *m/z* (%) = 417 (16) [M⁺],

389 (1), 361 (16), 333 (26), 305 (33), 278 (80), 253 (100), 237 (27), 222 (55), 199 (24), 187 (15) [Fc⁺].

3.5.2. (OC)₄Mo=C[(4,5-η²)-NHCH₂CH=CH₂]Fc (4b)

M.p. 115 °C (dec.) (lit. [19]: no m.p. quoted); Yield: 553 mg (60%). ¹H NMR (300.13 MHz, acetone-*d*₆): δ = 3.56 (dd, ³J = 9.2, ²J = 1.2 Hz, 1H, H^{CH₂}), 3.71 (dd, ³J = 14.1, ²J = 1.2 Hz, 1H, H^{CH₂}), 4.08 (m, 1H, H^{=CH₂}), 4.20 (m, 1H, H^{=CH₂}), 4.26 (s, 5H, H^{Cp}), 4.59 (dvt, ⁴J = 2.6, ³J = 1.4 Hz, 1H, H^{3,4-Fc}), 4.62 (dvt, ⁴J = 2.6, ³J = 1.4 Hz, 1H, H^{3,4-Fc}), 4.82 (dvt, ⁴J = 2.6, ³J = 1.4 Hz, 1H, H^{2,5-Fc}), 4.88 (dvt, ⁴J = 2.6, ³J = 1.4 Hz, 1H, H^{2,5-Fc}), 5.26 (dddd, ³J = 17.4, 14.1, 12.4, 9.2 Hz, 1H, H^{CH}), 9.83 (br, 1H, H^{NH}). IR (ATR): 3325 cm⁻¹ [ν(NH)], 2013/1916/1903/1823/1798 [ν(Mo(CO)₄)], 1545 [ν(C=C)], 1435 [ν(Cp)]. EI-MS: *m/z* (%) = 461 (17) [M⁺], 433 (2), 405 (6), 377 (24), 349 (44), 320 (18), 293 (9), 265 (20), 253 (100), 226 (22), 211 (28), 199 (33), 187 (16) [Fc⁺]. Anal. Calc. for C₁₈H₁₅FeMoNO₄ (461.1): C, 46.89; H, 3.28; N, 3.04. Found: C, 46.94; H, 3.20; N, 2.97%.

3.5.2.1. X-ray crystal structure determination of **4b**. Formula C₁₈H₁₅FeMoNO₄, molar mass 461.10 g mol⁻¹, crystal size 0.06 × 0.11 × 0.54 mm, *a* = 15.333(2), *b* = 8.7140(10), *c* = 12.9880(10) Å, α = 90°, β = 94.170(7)°, γ = 90°, *V* = 1730.8(3) Å³, *T* = 193 K, *d*_{calc} = 1.770 g cm⁻³, μ = 1.584 mm⁻¹, *Z* = 4, monoclinic, space group *P2*₁/*c*, STOE IPDS I diffractometer, λ = 0.71069 Å, θ-range 1.3–26.2°; ωϕ-scans, index ranges 0 ≤ *h* ≤ 18, –10 ≤ *k* ≤ 0, –16 ≤ *l* ≤ 15, 3404 collected reflections, 3404 independent reflections [*I* > 2σ(*I*)], 250 refined parameters, absorption correction by ψ-scans. Structure solution: direct methods (SIR97), structure refinement: full-matrix least-squares on *F*² (SHELXL97), *R* = 0.0232 [*w* = 1/σ²(*F*_o) + (0.0389*P*)²] where *P* = (*F*_o² + 2*F*_c²)/3, *wR*₂ = 0.0625, largest difference in peak and hole 0.32 and –0.60 e Å⁻³ (see Table 3).

3.5.3. (OC)₄W=C[(4,5-η²)-NHCH₂CH=CH₂]Fc (4c)

M.p. 128 °C (dec.); Yield: 758 mg (69%). ¹H NMR (300.13 MHz, acetone-*d*₆): 3.22 (dd, ³J = 13.3, ²J = 1.4 Hz, 1H, H^{CH₂}), 3.29 (dd, ³J = 9.3, ²J = 1.4 Hz, 1H, H^{CH₂}), 4.09 (m, 1H, H^{=CH₂}), 4.26 (s, 5H, H^{Cp}), 4.44 (m, 1H, H^{=CH₂}), 4.60 (dvt, ⁴J = 2.6, ³J = 1.2 Hz, 1H, H^{3,4-Fc}), 4.63 (dvt, ⁴J = 2.6, ³J = 1.2 Hz, 1H, H^{3,4-Fc}), 4.80 (dvt, ⁴J = 2.6, ³J = 1.2 Hz, 1H, H^{2,5-Fc}), 4.86 (dvt, ⁴J = 2.6, ³J = 1.2 Hz, 1H, H^{2,5-Fc}), 4.87 (m, 1H, H^{CH}), 10.0 (br, 1H, H^{NH}). IR (ATR): 3328 cm⁻¹ [ν(NH)], 2011/1914/1902/1823/1794 [ν(W(CO)₄)], 1545 [ν(C=C)], 1437 [ν(Cp)]. EI-MS: *m/z* (%) = 549 (47) [M⁺], 521 (1), 493 (16), 465 (38), 437 (100), 408 (26), 369 (20), 351 (16), 314 (11), 287 (7), 218 (6), 121 (10), 56 (16) [Fe⁺]. Anal. Calc. for C₁₈H₁₅FeNO₄W (549.0): C, 39.38; H, 2.75; N, 2.55. Found: C, 39.44; H, 2.68; N, 2.43%.

3.5.3.1. X-ray crystal structure determination of **4c**. Formula C₁₈H₁₅FeNO₄W, molar mass 549.00 g mol⁻¹, crystal size

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of the non-hydrogen atoms of **4b**

| Atom | x | y | z | U_{eq}^a |
|-------|-------------|------------|-------------|-------------------|
| Mo(1) | 0.16735(1) | 0.44591(3) | 0.65280(2) | 0.0279(1) |
| Fe(1) | 0.37425(2) | 0.03544(4) | 0.70656(3) | 0.0269(1) |
| O(1) | 0.11862(17) | 0.7746(2) | 0.5693(2) | 0.0544(8) |
| O(2) | 0.2234(2) | 0.5604(4) | 0.8767(2) | 0.0719(10) |
| O(3) | 0.36346(15) | 0.5164(3) | 0.60381(19) | 0.0507(8) |
| O(4) | -0.0198(2) | 0.4153(5) | 0.7399(3) | 0.0941(15) |
| N(1) | 0.14615(16) | 0.1041(3) | 0.6161(2) | 0.0351(8) |
| C(1) | 0.1366(2) | 0.6553(3) | 0.6029(2) | 0.0378(9) |
| C(2) | 0.2035(2) | 0.5180(4) | 0.7951(3) | 0.0455(11) |
| C(3) | 0.2933(2) | 0.4873(3) | 0.6196(2) | 0.0366(9) |
| C(4) | 0.0459(2) | 0.4216(4) | 0.7078(3) | 0.0515(12) |
| C(5) | 0.19386(17) | 0.1967(3) | 0.6762(2) | 0.0269(8) |
| C(6) | 0.25763(17) | 0.1190(3) | 0.7474(2) | 0.0271(8) |
| C(7) | 0.32876(18) | 0.1916(3) | 0.8067(2) | 0.0283(8) |
| C(8) | 0.37731(19) | 0.0773(4) | 0.8624(2) | 0.0335(8) |
| C(9) | 0.33799(19) | -0.0671(4) | 0.8397(2) | 0.0341(8) |
| C(10) | 0.26438(18) | -0.0435(3) | 0.7684(2) | 0.0307(8) |
| C(11) | 0.0733(2) | 0.1577(4) | 0.5458(3) | 0.0412(10) |
| C(12) | 0.0878(2) | 0.3200(3) | 0.5115(2) | 0.0366(9) |
| C(13) | 0.1642(2) | 0.3650(4) | 0.4746(2) | 0.0411(10) |
| C(14) | 0.3838(2) | 0.0811(4) | 0.5531(2) | 0.0423(10) |
| C(15) | 0.4552(2) | 0.1475(4) | 0.6127(2) | 0.0426(10) |
| C(16) | 0.5007(2) | 0.0278(4) | 0.6667(2) | 0.0454(10) |
| C(17) | 0.4576(2) | -0.1125(4) | 0.6410(3) | 0.0459(10) |
| C(18) | 0.3850(2) | -0.0790(4) | 0.5706(2) | 0.0415(10) |

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of the non-hydrogen atoms of **4c**

| Atom | x | y | z | U_{eq}^a |
|-------|----------|----------|----------|-------------------|
| W(1) | 0.16732 | 0.05382 | 0.15371 | 0.0223 |
| Fe(1) | 0.37391 | 0.46534 | 0.20625 | 0.0227 |
| O(1) | 0.11774 | -0.27489 | 0.06829 | 0.0479 |
| O(2) | 0.22420 | -0.05867 | 0.37777 | 0.0652 |
| O(3) | 0.36384 | -0.01687 | 0.10473 | 0.0443 |
| O(4) | -0.02010 | 0.08491 | 0.24000 | 0.0813 |
| N(1) | 0.14504 | 0.39661 | 0.11542 | 0.0289 |
| C(1) | 0.13555 | -0.15569 | 0.10311 | 0.0328 |
| C(2) | 0.20334 | -0.01709 | 0.29639 | 0.0378 |
| C(3) | 0.29313 | 0.01083 | 0.12041 | 0.0306 |
| C(4) | 0.04615 | 0.07857 | 0.20884 | 0.0457 |
| C(5) | 0.19255 | 0.30264 | 0.17523 | 0.0213 |
| C(6) | 0.25669 | 0.38193 | 0.24630 | 0.0214 |
| C(7) | 0.32793 | 0.30807 | 0.30619 | 0.0245 |
| C(8) | 0.37667 | 0.42443 | 0.36203 | 0.0276 |
| C(9) | 0.33695 | 0.56865 | 0.33862 | 0.0288 |
| C(10) | 0.26406 | 0.54456 | 0.26703 | 0.0267 |
| C(11) | 0.07272 | 0.34176 | 0.04544 | 0.0337 |
| C(12) | 0.08784 | 0.17827 | 0.01347 | 0.0286 |
| C(13) | 0.16584 | 0.13226 | -0.02344 | 0.0324 |
| C(14) | 0.38459 | 0.41943 | 0.05314 | 0.0371 |
| C(15) | 0.45568 | 0.35311 | 0.11287 | 0.0373 |
| C(16) | 0.50038 | 0.47442 | 0.16718 | 0.0394 |
| C(17) | 0.45799 | 0.61274 | 0.14106 | 0.0398 |
| C(18) | 0.38509 | 0.57998 | 0.07044 | 0.0386 |

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

0.19 × 0.46 × 0.52 mm, $a = 15.2950(10)$, $b = 8.6760(10)$, $c = 12.9865(10)$ Å, $\alpha = 90^\circ$, $\beta = 94.170(4)^\circ$, $\gamma = 90^\circ$, $V = 1718.7(3)$ Å³, $T = 193$ K, $d_{\text{calc}} = 2.122$ g cm⁻³, $\mu = 7.554$ mm⁻¹, $Z = 4$, monoclinic, space group $P2_1/c$, STOE IPDS I diffractometer, $\lambda = 0.71069$ Å, Θ -range 1.33 – 25.97° ; ω - Φ -scans, index ranges $-18 \leq h \leq 18$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$, 3345 collected reflections, 3248 independent reflections [$I > 2\sigma(I)$], 250 refined parameters, absorption correction by ψ -scans. Structure solution: direct methods (SIR97), structure refinement: full-matrix least-squares on F^2 (SHELXL97), $R = 0.0260$ [$w = 1/\sigma^2(F_o) + (0.0294P)^2$] where $P = (F_o^2 + 2F_c^2)/3$, $wR_2 = 0.0614$, largest difference in peak and hole 0.554 and -2.143 e Å⁻³ (see Table 4).

3.5.4. $(OC)_4Cr=C[(4,5-\eta^2)-NHCH_2CH=CHCH_2OH]Fc$ (**5a**)

M.p. 65 °C (dec.); Yield: 653 mg (73%). ¹H NMR (300.13 MHz, acetone- d_6): $\delta = 3.57$ (m, 1H, H^{CH₂O}), 4.07 (m, 1H, H^{CH}), 4.28 (s, 5H, H^{Cp}), 4.30 (m, 2H, H^{NCH₂}), 4.31 (m, 1H, H^{CH₂O}), 4.38 (br, 1H, H^{OH}), 4.57 (vt, 1H, H^{3,4-Fc}), 4.58 (vt, 1H, H^{3,4-Fc}), 4.74 (vt, 1H, H^{2,5-Fc}), 4.84 (vt, 1H, H^{2,5-Fc}), 4.92 (m, 1H, H^{CH}), 9.7 (br, 1H, H^{NH}). IR (ATR): 3291 cm⁻¹ [$\nu(\text{OH})$], 3229 [$\nu(\text{NH})$], 2003/1908/1891/1851/1823 [$\nu(\text{Cr}(\text{CO})_4$)], 1551 [$\nu(\text{C}=\text{C})$], 1440 [$\nu(\text{Cp})$]. EI-MS: m/z (%) = 447 (2) [M^+], 419 (1), 396 (11), 391 (1), 363 (1), 335 (3), 265 (13), 211 (46), 201 (42), 187 (35) [Fc^+], 121 (94), 56 (100) [Fe^+]. Anal. Calc. for C₁₉H₁₇CrFeNO₅ (447.2): C, 51.03; H, 3.83; N, 3.13. Found: C, 50.92; H, 3.81; N, 3.19%.

3.5.5. $(OC)_4Mo=C[(4,5-\eta^2)-NHCH_2CH=CHCH_2OH]Fc$ (**5b**)

M.p. 60 °C (dec.); Yield: 589 mg (60%). ¹H NMR (300.13 MHz, acetone- d_6): $\delta = 3.97$ (m, 1H, H^{OCH₂}), 4.20 (m, 1H, H^{NCH₂}), 4.28 (m, 1H, H^{NCH₂}), 4.29 (s, 5H, H^{Cp}), 4.32 (br, 1H, H^{OH}), 4.39 (m, 1H, H^{OCH₂}), 4.60 (vt, 1H, H^{3,4-Fc}), 4.61 (vt, 1H, H^{3,4-Fc}), 4.87 (vt, 2H, H^{2,5-Fc}), 4.72 (m, 1H, H^{CH}), 5.34 (m, 1H, H^{CH}), 10.0 (br, 1H, H^{NH}). IR (ATR): 3300 cm⁻¹ [$\nu(\text{OH})$], 3220 [$\nu(\text{NH})$], 2017/1910/1898/1848 [$\nu(\text{Mo}(\text{CO})_4$)], 1551 [$\nu(\text{C}=\text{C})$], 1438 [$\nu(\text{Cp})$]. EI-MS: m/z (%) = 491 (3) [M^+], 463 (9), 435 (2), 407 (1), 317 (6), 263 (10), 199 (26), 187 (17) [Fc^+], 129 (9), 121 (100), 56 (77) [Fe^+]. Anal. Calc. for C₁₉H₁₇FeMoNO₅ (491.1): C, 46.46; H, 3.49; N, 2.85. Found: C, 46.38; H, 3.40; N, 2.69%.

3.5.6. $(OC)_4W=C[(4,5-\eta^2)-NHCH_2CH=CHCH_2OH]Fc$ (**5c**)

M.p. 72 °C (dec.); Yield: 799 mg (69%). ¹H NMR (300.13 MHz, acetone- d_6): $\delta = 3.83$ (m, 1H, H^{CH₂O}), 4.20 (br, 1H, H^{OH}), 4.28 (m, 1H, H^{NCH₂}), 4.30 (s, 5H, H^{Cp}), 4.31 (m, 1H, H^{CH}), 4.37 (m, 1H, H^{NCH₂}), 4.41 (m, 1H, H^{CH₂O}), 4.61 (vt, 1H, H^{3,4-Fc}), 4.64 (vt, 1H, H^{3,4-Fc}), 4.84 (vt, 2H, H^{2,5-Fc}), 4.92 (m, 1H, H^{CH}), 10.2 (br, 1H, H^{NH}). IR (ATR): 3314 cm⁻¹ [$\nu(\text{OH})$], 3242 [$\nu(\text{NH})$], 2014/1879/1837 [$\nu(\text{W}(\text{CO})_4$)], 1531 [$\nu(\text{C}=\text{C})$], 1438 [$\nu(\text{Cp})$]. EI-MS: m/z (%) = 551 (1) [$\text{M}^+ - \text{CO}$], 495 (1), 467 (2), 350 (78), 298 (54), 266 (100), 199 (47), 134 (92), 121 (73), 56 (79) [Fe^+]. Anal. Calc. for C₁₉H₁₇FeNO₅W (579.05): C, 39.41; H, 2.96; N, 2.42. Found: C, 39.48; H, 3.06; N, 2.29%.

3.6. DFT calculations

The density functional single point calculations of **4a** and **4b** were performed with the GAMESS 2001 suite of programs [23] using the geometry obtained from the X-ray single crystal structural analyses, the B3LYP [25,26] density functional and the N21 basis set, augmented with standard polarization functions on the non-hydrogen atoms [27]. Calculated frontier orbital energies: **4a**: $E_{\text{HOMO}} = -0.163$ eV, $E_{\text{HOMO}-1} = -0.168$ eV, $E_{\text{HOMO}-2} = -0.183$ eV, $E_{\text{HOMO}-3} = -0.212$ eV; **4b**: $E_{\text{HOMO}} = -0.180$ eV, $E_{\text{HOMO}-1} = -0.193$ eV, $E_{\text{HOMO}-2} = -0.209$ eV, $E_{\text{HOMO}-3} = -0.213$ eV.

4. Supplementary material

Crystallographic data for the structures of **4b** and **4c** have been deposited with the Cambridge Crystallographic Data Centre [CCDC Nos. 278098 (**4b**) and 278099 (**4c**)]. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code+1223 336 033, e-mail: teched@chemcryst.cam.ac.uk).

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