

Improved approaches and structures of new ferrocenyl carbene complexes of chromium, tungsten, and molybdenum

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Abstract

Ferrocenyllithium reacts with $M(\text{CO})_6$ ($M = \text{Cr}, \text{W}, \text{Mo}$) in *THF* to give, after alkylation at oxygen, the corresponding carbene complexes **3a–c** in good yield. Complexes **3a,b** were characterized by X-ray analysis. These complexes react with pentylamine to give the corresponding aminocarbene complexes **7a–c** and with allylamine to give, in the case of chromium and tungsten, the corresponding and expected aminocarbene complexes **8a,b**, and for molybdenum, complex **9c** in which the double bond is already coordinated to the metal. **8a,b** could be converted in **9a,b** in excellent yield. The structure of **9a** could be confirmed by an X-ray analysis. Alkylations at nitrogen could be carried on complex **9c** as well as on complexes **9a,b**.

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Keywords: Carbene complexes; Ferrocene; Heterobimetallic complexes

1. Introduction

The synthesis and applications of ferrocenyl-containing ligands is a rapidly expanding field since they can be used in catalytic transformations of organic compounds when associated with a second transition metal. It has indeed been found that these new catalysts show activities, diastereo- and enantioselectivities very often far beyond all those containing classical organic ligands [1]. One way among many others to modify, and possibly introduce chirality in ferrocene complexes would be to start from ferrocenyl carbene complexes. Such approaches have already been used by several groups either to synthesize new complexes or to use the carbene

moiety as a building block for the synthesis of organic compounds [2]. As part of a project directed to the synthesis and modifications of ferrocenyl carbene complexes developed in our Laboratories, we became involved in the preparation of ferrocenyl aminocarbene complexes tethered to double and triple bonds. The classical method to introduce such functions would be to start from alkoxy carbene complexes and react them with unsaturated amines [3]. The purpose of this paper is to describe successful routes to the starting aminocarbene complexes.

2. Results and discussion

Although many ferrocenyl carbene complexes have been described in the literature [2], their yields of formation are very often not satisfactory. The goal of this

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paper is thus first to describe improved approaches to our starting materials, ferrocenylalkoxycarbene complexes of tungsten, chromium and molybdenum; second to carry out the aminolysis of these carbene complexes with saturated as well as unsaturated amines; third to describe the results of the attempts to coordinate the double bonds to the metal center, which led indeed to bidentate alkene ferrocenyl aminocarbene complexes the structure of which was established by X-ray crystallography.

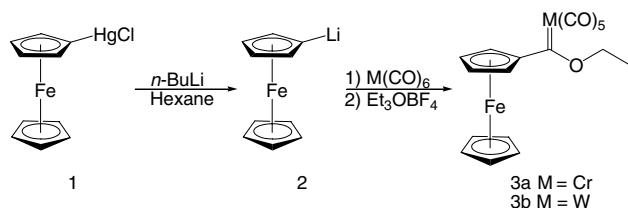
2.1. Improved syntheses and X-ray structures of alkoxy ferrocenyl carbene complexes

Early approaches to the very simple ferrocenyl carbene complexes were described by Connor [2a] who used the classical Fischer method for the general synthesis of alkoxy carbene complexes. Thus, reaction of ferrocenyllithium **2** obtained from ferrocenylmercury chloride **1** with $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ followed by alkylation at oxygen led to the expected complexes **3a** and **3b** in, respectively, 47% and 40% yield (Scheme 1).

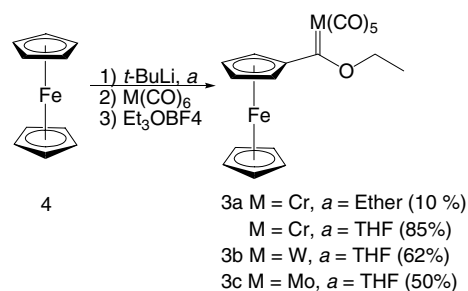
A first improvement of the method was achieved by Zora and coworkers [2f]. Indeed, these authors replaced the expensive and unfriendly ferrocenylmercury chloride by ferrocene **4**. Its reaction with *t*-BuLi in diethyl ether led indeed to ferrocenyllithium, and thus to the alkoxy carbene complex **3a** in 72% yield. However, attempts to reproduce this reaction under the given conditions led only in our hands to very low (10%) yields of the expected complex **3a**. A great improvement giving reproducible results was however observed upon changing the nature of the solvent. Use of suspensions of the metal carbonyls in THF instead of Et_2O led indeed to the known complexes **3a,b** ($\text{M} = \text{Cr}, \text{W}$), and to the unknown complex **3c** ($\text{M} = \text{Mo}$, brown solid, m.p. 133°C) in, respectively, 85%, 62% and 50% yields (Scheme 2).

Since, to the best of our knowledge, such carbene complexes had not been structurally characterized, the X-ray structure determination of **3a** and **3b** was undertaken. The ORTEP views of these complexes appear in Figs. 1 and 2.

According to the gathered data, no significant differences in the geometry and bond distances around the carbene function can be noticed in going from a classical



Scheme 1.



Scheme 2.

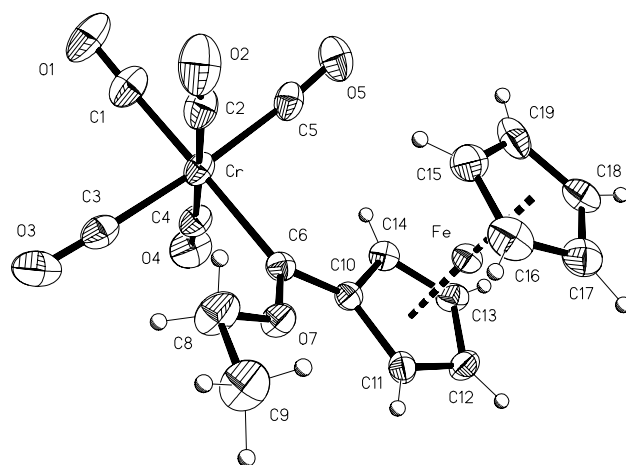


Fig. 1. X-ray crystal structure of complex **3a**. Ellipsoids are shown at the 30% probability level.

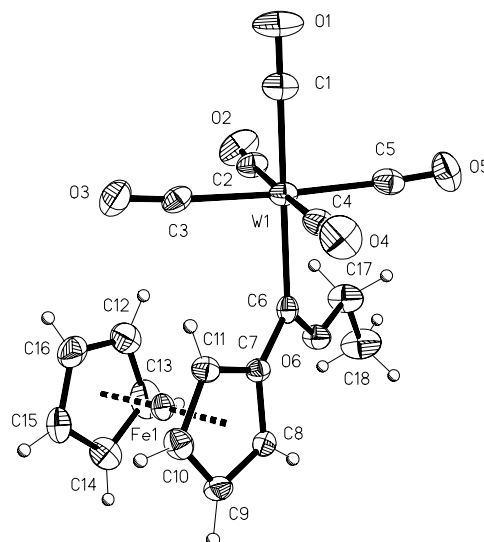


Fig. 2. X-ray crystal structure of complex **3b**. Ellipsoids are shown at the 30% probability level.

to a ferrocene-substituted alkoxy carbene complex since neither the metal–carbene carbon nor the oxygen–carbene carbon distances were affected by the introduction of the ferrocenyl ligand (Tables 1 and 2). It is to

Table 1
Selected bond lengths (Å) and selected bond angles (°) for **3a**

Selected bond lengths (Å)							
Cr–C1	1.876(3)	Cr–C3	1.897(3)	Cr–C4	1.898(3)	Cr–C2	1.904(3)
Cr–C5	1.915(3)	Cr–C6	2.084(2)	C6–O7	1.317(2)	C6–C10	1.452(3)
O7–C8	1.438(3)	C10–C14	1.441(3)	C10–C11	1.447(3)	C1–O1	1.135(3)
C2–O2	1.132(3)	C3–O3	1.135(3)	C4–O4	1.135(3)	C5–O5	1.128(3)
Selected bond angles (°)							
C1–Cr–C6	176.82(10)	C14–C10–C11	105.53(11)	C4–Cr–C6	87.26(9)	C10–C6–Cr	125.48(15)
C5–Cr–C6	92.86(10)	O7–C6–C10	105.58(17)	O7–C6–Cr	128.80(15)	C11–C10–C6	124.84(19)
C3–Cr–C6	92.11(9)	C14–C10–C6	128.7(2)	C2–Cr–C6	94.23(9)		

Table 2
Selected bond lengths (Å) and selected bond angles (°) for **3b**

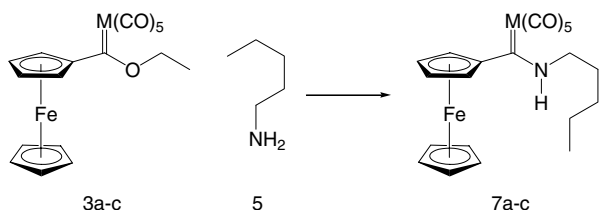
Selected bond lengths (Å)							
W1–C1	2.018(5)	W1–C3	2.021(6)	W1–C5	2.034(7)	W1–C2	2.043(5)
W1–C4	2.054(5)	W1–C6	2.215(4)	C6–C7	1.465(6)	C7–C11	1.410(6)
C7–C8	1.426(5)	C1–O1	1.136(5)	C2–O2	1.135(5)	C3–O3	1.140(6)
C4–O4	1.112(5)	C5–O5	1.144(7)	C6–O6	1.135(5)		
Selected bond angles (°)							
C1–W1–C3	86.2(2)	C3–W1–C2	89.4(2)	C2–W1–C6	94.97(17)	C3–W1–C5	175.44(18)
C1–W1–C2	89.0(2)	C5–W1–C4	87.4(2)	C4–W1–C6	86.99(17)	C2–W1–C4	178.04(18)
C5–W1–C2	92.5(2)	C3–W1–C4	90.6(2)	O6–C6–C7	105.9(4)	C1–W1–C6	175.98(18)
C1–W1–C4	89.1(2)	C3–W1–C6	92.60(17)	O6–C6–W1	128.8(3)	C8–C7–C6	124.5(4)
C1–W1–C5	89.2(2)	C5–W1–C6	91.41(18)	C7–C6–W1	125.2(3)	C11–C7–C6	127.9(4)

notice that they both crystallized in a non-centrosymmetric space group.

2.2. Synthesis of the corresponding ferrocenyl aminocarbene complexes **7a–c** and **8a–c**

In order to carry out the aminolysis of the complexes **3a–c** either with the saturated or the unsaturated amines **5** and **6**, the classical method of Fischer [3], which had already been used by Connor in the case of ferrocenyl-carbene complexes, [2f] was applied. This led with pentylamine **5** to the complexes **7a–c** in excellent 93%, and twice 94% yields (Scheme 3). The physical data of these complexes are in agreement with the proposed structures (see Section 3).

Similarly, interaction of complexes **3a,b** with allylamine **6** led to the expected complexes **8a,b** in, respectively, 94% and 62% yield (Scheme 4) giving in the ¹H and ¹³C NMR spectra, the typical signals for a free, terminal, monosubstituted double bond.

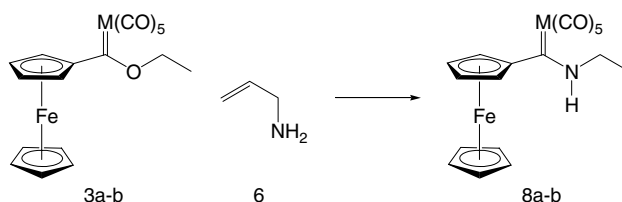


Scheme 3.

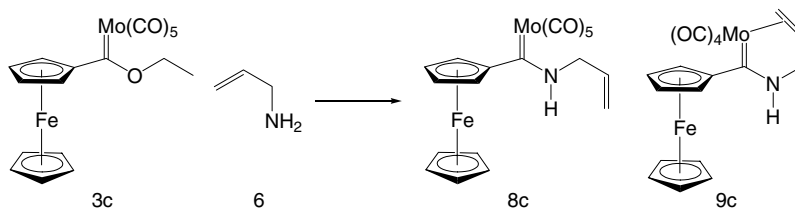
However, in the case of the molybdenum complex **3c**, the same reaction led to two new complexes, complex **8c** (13%) in which, according to the mass spectrum and the NMR data, five carbonyl groups are still present on the metal, and complex **9c** (86%), bearing only four CO groups, and thus, according to the NMR spectra, the double bond is coordinated to the metal. Thus, a spontaneous coordination of the double bond of **8c** took place (Scheme 5).

2.3. Attempts to synthesize complexes **9a,b**: X-ray structure of complex **9a**

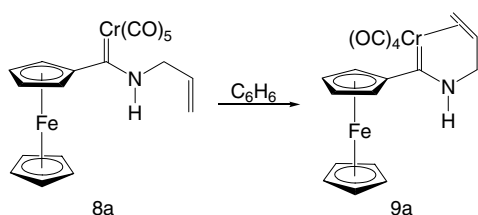
Thermolysis in benzene is a classical method to convert eta-2 alkene-carbene complexes of the Fischer-type into their counterpart eta-4 complexes. This method was therefore also followed in the case of complexes **8a,b**. Thus, heating complex **8a** in refluxing benzene led almost quantitatively (96%) to a new orange complex **9b**, m.p. 160–162 °C (Scheme 6).



Scheme 4.



Scheme 5.



Scheme 6.

Both the mass spectrum and the NMR data confirmed the coordination of the double bond, the signals for the vinylic protons being shifted upfield, from 6.14 to 4.70 ppm (CH=CH₂), and from 5.51 to 3.14 and 2.88 ppm (CH=CH₂). An X-ray structure determination confirmed indeed structure **9a**: an ORTEP projection appears in Fig. 3.

The most important bond distances (Tables 3 and 4) could be compared to those observed in related chromium aminocarbene complexes devoid of the ferrocenyl substituent: no significant differences could be detected, neither in the geometry of the carbene function, nor in the bond distances between the metal and the coordinated double bond [3] (Table 3).

Surprisingly, when the same reaction was attempted on complex **8b**, no coordination of the double bond was observed, the starting material being recovered even after extended periods of reflux in benzene.

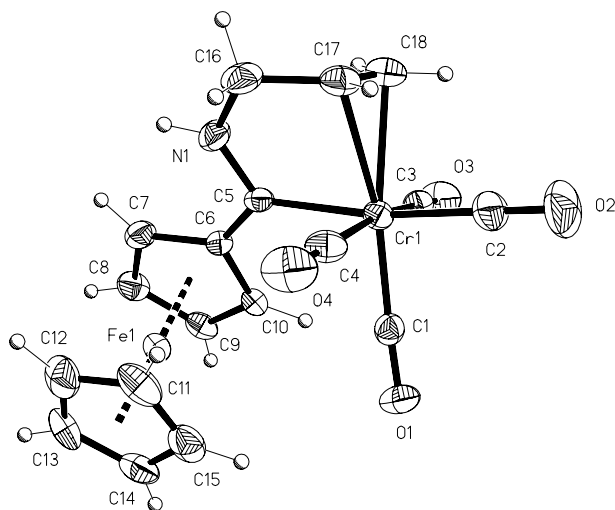


Fig. 3. X-ray crystal structure of complex **9a**. Ellipsoids are shown at the 30% probability level.

2.4. Alkylation at nitrogen: synthesis of complexes **10a, c** and **11b**

Alkylations at nitrogen of monosubstituted aminocarbene complexes is classically carried out by deprotonation with LDA followed by reaction with an alkyl halide [3]. Under such conditions, and in the presence of methyl iodide, complex **9b** underwent a clean, high yielding transformation (90%) into complex **10** (Scheme 7), the structure of which was confirmed both by mass and NMR spectroscopies which indicated indeed the presence of a new methyl group with a signal at δ 3.51 ppm.

A similar alkylation could also be carried out on complexes **9a** and **9c** although the double bond was already coordinated to the metal: the expected alkene–carbene complexes **11a** and **11c** were isolated in, respectively, 85% and 83% yields (Scheme 8).

The structure of **11a** was confirmed by X-ray diffraction analysis (Fig. 4). Comparing the bond distances and bond angles of **9a** and **11a** (Tables 3 and 4), we can observe some slight differences in the geometry of the aminocarbene function. The bond angle C3–Cr1–C4 is increased in **11a** (**9a**: 170.14 (12)°; **11a**: 172.30(14)°). In both structures, the double bond is in an equatorial position *cis* with respect to the carbene carbon C5, but in **11a** the bond angles C5–Cr1–C18 and C5–Cr1–C19 are slightly enlarged whereas the bond angle of C5–N1–C17 decreased by 3.5°. These small changes in the geometry can be attributed to the presence of the extra methyl group on the nitrogen atom in **11a**.

Work is now progressing towards the use of these new aminocarbene complexes for the synthesis of ferrocene-containing ligands. As a further step, attempts will also be made to introduce triple-bond containing amines in the precursor ferrocenyl alkoxy carbene complexes.

3. Experimental

3.1. Chemical and methods

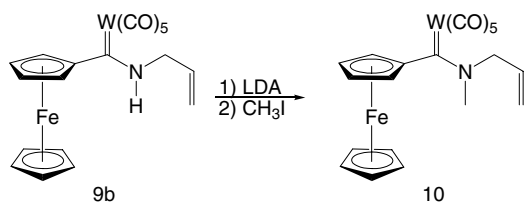
¹H NMR and ¹³C NMR spectra were recorded on a JEOL 300 spectrometer, using CDCl₃ as solvent and TMS as internal reference. IR spectra were performed on a Perkin–Elmer 283 B or 1420 spectrometer. The

Table 3
Selected bond lengths (Å) and selected bond angles (°) for **9a**

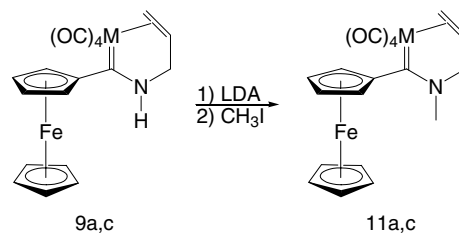
Selected bond lengths (Å)							
Cr1–C1	1.847(3)	Cr1–C17	2.284(3)	O3–C3	1.143(3)	C5–C6	1.456(3)
Cr1–C2	1.862(3)	Cr1–C18	2.290(2)	O4–C4	1.148(3)	C6–C10	1.424(3)
Cr1–C3	1.866(3)	O1–C1	1.159(3)	N1–C5	1.322(3)	C6–C7	1.453(3)
Cr1–C4	1.867(3)	O2–C2	1.147(3)	N1–C16	1.455(3)	C16–C17	1.497(3)
Cr1–C5	2.071(2)	C17–C18	1.360(3)				
Selected bond angles (°)							
C1–Cr1–C2	90.14(12)	C3–Cr1–C5	89.27(10)	C1–Cr1–C17	164.21(11)	C2–Cr1–C18	88.58(12)
C1–Cr1–C3	85.18(11)	C4–Cr1–C5	87.62(11)	C3–Cr1–C17	109.96(11)	C3–Cr1–C18	75.99(11)
C2–Cr1–C3	92.90(12)	C5–N1–C16	122.1(2)	C2–Cr1–C5	170.75(11)	C5–Cr1–C18	83.22(10)
C1–Cr1–C4	86.06(11)	N1–C5–C6	112.8(2)	C4–Cr1–C17	78.48(11)	C4–Cr1–C18	112.88(11)
C2–Cr1–C4	91.65(13)	N1–C5–Cr1	115.71(19)	C5–Cr1–C17	77.63(10)	C1–Cr1–C18	161.06(11)
C1–Cr1–C5	98.75(10)	C3–Cr1–C4	170.14(12)	C2–Cr1–C17	93.19(12)	C10–C6–C7	105.7(2)
C10–C6–C5	125.5(2)	C7–C6–C5	128.9(2)				

Table 4
Selected bond lengths (Å) and selected bond angles (°) for **11a**

Selected bond lengths (Å)							
Cr1–C1	1.844(3)	Cr1–C18	2.242(3)	O4–C4	1.145(3)	C5–C6	1.463(4)
Cr1–C2	1.849(3)	Cr1–C19	2.276(4)	N1–C5	1.317(3)	C6–C10	1.442(4)
Cr1–C3	1.881(3)	O1–C1	1.150(3)	N1–C16	1.467(4)	C6–C7	1.448(4)
Cr1–C4	1.874(3)	O2–C2	1.152(3)	N1–C17	1.468(4)	C17–C18	1.493(5)
Cr1–C5	2.107(3)	O3–C3	1.139(3)			C18–C19	1.348(5)
Selected bond angles (°)							
C1–Cr1–C2	89.02(13)	C3–Cr1–C5	88.79(12)	C1–Cr1–C18	163.21(14)	C2–Cr1–C19	90.54(16)
C1–Cr1–C3	86.14(14)	C4–Cr1–C5	90.57(11)	C3–Cr1–C19	112.19(15)	C3–Cr1–C18	77.92(14)
C2–Cr1–C3	90.17(14)	C5–N1–C16	126.2(3)	C2–Cr1–C5	174.02(12)	C5–Cr1–C19	84.41(14)
C1–Cr1–C4	86.31(13)	N1–C5–C6	119.2(2)	C4–Cr1–C19	75.37(15)	C4–Cr1–C18	109.44(14)
C2–Cr1–C4	91.24(13)	N1–C5–Cr1	116.5(2)	C5–Cr1–C18	77.83(12)	C1–Cr1–C19	161.66(15)
C1–Cr1–C5	96.78(12)	C3–Cr1–C4	172.30(14)	C2–Cr1–C18	96.19(13)	C10–C6–C7	105.2(2)
C10–C6–C5	125.2(3)	C7–C6–C5	129.2(3)	C18–Cr1–C19	34.72(13)	C5–N1–C17	118.6(2)
C6–C5–Cr1	124.21(19)						



Scheme 7.



Scheme 8.

FAB spectra were obtained on a JEOL JMS SX 102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using a 6 keV Xenon atoms. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA Mass spectrometer operated in the positive ion mode. The acquisition conditions were ion source temperature 230 °C, ionization energy 70 eV, emission current 0.14 μ A and ionization current 100 μ A. Mass measurements in FAB are performed at 10000 resolution using electrical field scans and the

polyethylene glycol ions as reference material. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under nitrogen atmosphere in carefully dried glassware. THF was distilled from sodium-benzo phenone under argon or nitrogen atmosphere. Column chromatography was performed with Merck silica gel (70–230 mesh) using ethyl acetate: hexane in different ratios as eluent.

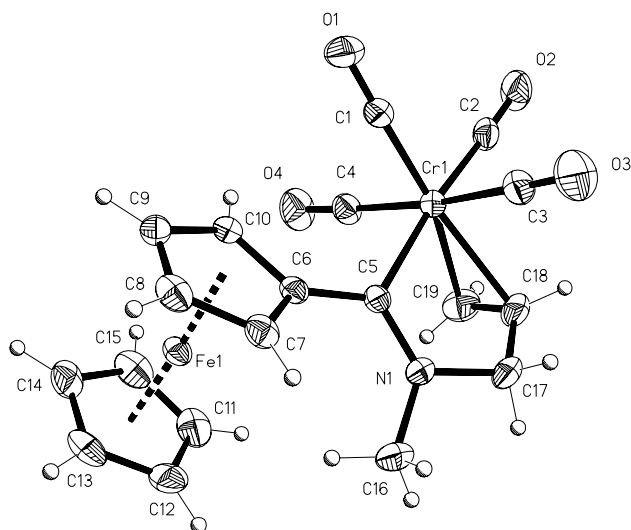


Fig. 4. X-ray crystal structure of complex **11a**. Ellipsoids are shown at the 30% probability level.

3.2. Preparation of ferrocenylated group 6 metal Fischer-type carbenes

[(Ethoxy)(ferrocenyl)methylidene]pentacarbonylchromium(0) 3a: To a solution of ferrocene (2 g, 10.7 mmol) in anhydrous THF (20 ml) was added at 0 °C 6.3 ml of a 1.7 M solution of *t*-butyllithium in pentane (10.71 mmol), the mixture was stirred 15 min at this temperature then allowed to warm at room temperature. The suspension was transferred by canula to a suspension of Cr(CO)₆ (1.17 g, 5.35 mmol) in THF (25 ml), the mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum, and then triethyloxonium tetrafluoroborate (1.52 g, 8 mmol) on ice/water was added. The mixture was stirred for 15 min then was extracted with CH₂Cl₂, the organic phase was washed with a saturated solution of NaHCO₃ then brine. The organic phase was dried with anhydrous sodium sulfate and the solvent was evaporated under vacuum then the mixture was purified by chromatography on silicagel using hexane as eluent to give 2.0 g of a brown solid (85%). ¹H NMR (CDCl₃): δ 5.00 (br m, 4H, subst Cp and CH₂O), 4.77 (br s, 2H, subst Cp), 4.22 (s, 5H, Cp), 1.60 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 329.7 (C=Cr), 223.0 (CrCO), 217.3 (CrCO), 93.6 (C_{ipso}, fc), 75.5 (OCH₂), 74.5 (CH, subst Cp), 72.3 (CH, subst Cp), 70.6 (Cp), 15.5 (CH₃). IR (KBr): ν/cm⁻¹ 2053 (CO), 1905 (CO). MS (FAB⁺): *m/z* 434 (M⁺), 378 (M⁺ – 2CO), 322 (M⁺ – 4CO).

[(Ethoxy)(ferrocenyl)methylidene]pentacarbonyl tungsten(0) 3b: The complex **3b** was obtained by a similar procedure, as a brown solid (62%). ¹H NMR (CDCl₃): δ 4.98 (br s, 2H, subst Cp), 4.85 (br m, 4H, subst Cp and CH₂O), 4.25 (s, 5H, Cp), 1.58 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 304.3 (C=W), 202.5

(WCO), 198.0 (WCO), 95.2 (C_{ipso}, fc), 78.1 (OCH₂), 75.0 (CH, subst Cp), 73.3 (CH, subst Cp), 70.8 (Cp), 15.4 (CH₃). IR (KBr): ν/cm⁻¹ 2061 (CO), 1900 (CO). MS (FAB⁺): *m/z* 565 (M⁺), 510 (M⁺ – 2CO), 482 (M⁺ – 3CO).

[(Ethoxy)(ferrocenyl)methylidene]pentacarbonylmolybdenum(0) 3c: The complex **3c** was obtained by a similar procedure, as a brown solid (50%). ¹H NMR (CDCl₃): δ 4.98 (br m, 4H, subst Cp and CH₂O), 4.81 (br s, 2H, subst Cp), 4.24 (s, 5H, Cp), 1.58 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 319.8 (C=Mo), 212.8 (MoCO), 206.4 (MoCO), 93.3 (C_{ipso}, fc), 77.1 (OCH₂), 74.9 (CH, subst Cp), 72.8 (CH, subst Cp), 70.6 (Cp), 15.4 (CH₃). IR (KBr): ν/cm⁻¹ 2063 (CO), 1982 (CO). MS (FAB⁺): *m/z* 480 (M⁺), 424 (M⁺ – 2CO), 394 (M⁺ – 3CO). HR-MS (FAB⁺) C₁₈H₁₄FeMoO₆: Calc. 479.9194. Found: 479.9212%.

3.3. Preparation of pentilaminocarbenes

[(Ferrocenyl)(pentylamine)methylidene]pentacarbonylchromium(0) 7a: To a solution of **1a** (1 g, 2.29 mmol) in anhydrous ether (10 ml) was added at room temperature 0.4 ml of pentylamine (5.17 mmol), then the reaction was stirred for overnight. The solvent was evaporated under vacuum and then the product was purified by chromatography on alumina using hexane as the eluent to give 1.00 g of an orange solid (94%). ¹H NMR (CDCl₃): δ 9.50 (s, 1H, NH), 4.45 (br s, 4H, subst Cp), 4.19 (s, 5H, Cp), 4.05 (m, 2H, NCH₂), 1.88 (m, 2H, NCH₂CH₂), 1.51 (m, 4H, CH₂CH₂CH₃), 1.0 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 270.5 (C=Cr), 223.6 (CrCO), 217.8 (CrCO), 99.4 (C_{ipso}, fc), 70.1 (CH, subst Cp), 69.4 (Cp), 68.4 (CH, subst Cp), 52.9 (NCH₂), 29.6 (NCH₂CH₂), 29.1 (CH₂CH₂CH₃), 22.5 (CH₂CH₃), 14.0 (CH₃). IR (KBr): ν/cm⁻¹ 2053 (CO), 1927 (CO). MS (FAB⁺): *m/z* 475 (M⁺). HR-MS (FAB⁺) C₂₁H₂₁CrFeNO₅: Calc. 475.0174. Found: 475.0191%.

[(Ferrocenyl)(pentylamine)methylidene]pentacarbonyl tungsten(0) 7b: The complex **7b** was obtained by a similar procedure, as an orange solid (94%). ¹H NMR (CDCl₃): δ 9.02 (s, 1H, NH), 4.54 (s, 2H, subst Cp), 4.50 (s, 2H, subst Cp), 4.20 (s, 5H, Cp), 3.92 (m, 2H, NCH₂), 1.83 (m, 2H, NCH₂CH₂), 1.49 (m, 4H, CH₂CH₂CH₃), 0.99 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 249.6 (C=W), 203.4 (WCO), 198.7 (WCO), 97.3 (C_{ipso}, fc), 70.9 (CH, subst Cp), 69.7 (Cp), 69.6 (CH, subst Cp), 55.2 (NCH₂), 29.6 (NCH₂CH₂), 29.0 (CH₂CH₂CH₃), 22.5 (CH₂CH₃), 14.0 (CH₃). IR (CHCl₃): ν/cm⁻¹ 2053 (CO), 1961 (CO). MS (EI⁺): *m/z* 607 (M⁺). HR-MS (FAB⁺) C₂₁H₂₁FeNO₅W: Calc. 607.0279. Found: 607.0296%.

[(Ferrocenyl)(pentylamine)methylidene]pentacarbonylmolybdenum(0) 7c: The complex **7c** was obtained by a similar procedure, as an orange solid (94%). ¹H NMR (CDCl₃): δ 9.10 (s, 1H, NH), 4.53

(s, 2H, subst Cp), 4.50 (s, 2H, subst Cp), 4.20 (s, 5H, Cp), 4.0 (m, 2H, NCH₂), 1.82 (m, 2H, NCH₂CH₂), 1.48 (m, 4H, CH₂CH₂CH₃), 1.0 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 261.5 (C=Mo), 213.6 (MoCO), 207.0 (MoCO), 96.0 (C_{ipso}, fc), 70.8 (CH, subst Cp), 69.6 (Cp), 69.2 (CH, subst Cp), 54.5 (NCH₂), 29.6 (NCH₂CH₂), 29.0 (CH₂CH₂CH₃), 22.5 (CH₂CH₃), 14.0 (CH₃). IR (CHCl₃): ν/cm⁻¹ 2061 (CO), 1977 (CO), 1931 (CO). MS (FAB⁺): *m/z* 521 (M⁺). HR-MS (FAB⁺) C₂₁H₂₁FeMoNO₅: Calc. 520.9823. Found: 520.9812%.

3.4. Preparation of allylaminocarbenes

[(*Allylamino*)(ferrocenyl)methylidene]pentacarbonylchromium(0) **8a**: To a solution of **3a** (0.5 g, 1.15 mmol) in anhydrous ether (15 ml) was added at room temperature 0.1 ml of allylamine (1.3 mmol), then the reaction was stirred for overnight. The solvent was evaporated under vacuum and then the product was purified by chromatography on silicagel using hexane–ethylacetate (4:1) as the eluent to give 0.48 g of an orange solid (94%). ¹H NMR (CDCl₃): δ 9.47 (br s, 1H NH), 6.14 (br s, 1H, CH=CH₂), 5.51 (br s, 2H, CH=CH₂), 4.71 (br s, 2H, NCH₂), 4.49 (br s, 4H, subst Cp), 4.21 (s, 5H, Cp). ¹³C{¹H} NMR (CDCl₃): δ 272.6 (C=Cr), 223.5 (CrCO), 217.7 (CrCO), 132.2 (CH=CH₂), 120.4 (CH=CH₂), 98.9 (C_{ipso}, fc), 70.4 (CH, subst Cp), 69.6 (Cp), 68.6 (CH, subst Cp), 55.3 (NCH₂). IR (KBr): ν/cm⁻¹ 3225 (NH), 2051 (CO), 1900 (CO). MS (FAB⁺): *m/z* 445 (M⁺), 417 (M⁺ – CO), 361 (M⁺ – 3CO), 333 (M⁺ – 4CO), 305 (M⁺ – 5CO), 267 (FcCCrNH). HR-MS (FAB⁺) C₁₉H₁₅CrFeNO₅: Calc. 444.9705. Found: 444.9721%.

[(*Allylamino*)(ferrocenyl)methylidene]pentacarbonyltungsten(0) **8b**: The complex **2b** was obtained by a similar procedure, as an orange solid (62%). ¹H NMR (CDCl₃): δ 9.00 (br s, 1H NH), 6.09 (m, 1H, CH=CH₂), 5.48 (m, 2H, CH=CH₂), 4.60–4.50 (m, 6H, NCH₂, subst Cp), 4.22 (s, 5H, Cp). ¹³C{¹H} NMR (CDCl₃): δ 251.6 (C=CW), 203.3 (WCO), 198.6 (WCO), 132.0 (CH=CH₂), 120.2 (CH=CH₂), 96.9 (C_{ipso}, fc), 71.2 (CH, subst Cp), 69.8 (Cp), 57.6 (NCH₂). IR (KBr): ν/cm⁻¹ 3316 (NH), 2059 (CO), 1903 (CO), 1869 (CO). MS (FAB⁺): *m/z* 577 (M⁺), 493 (M⁺ – 3CO), 465 (M⁺ – 4CO). HR-MS (FAB⁺) C₁₉H₁₅FeNO₅W: Calc. 576.9809. Found: 576.9898%.

[(*Allylamino*)(ferrocenyl)methylidene]pentacarbonylmolybdenum(0) **8c**: The complex **8c** was obtained by a similar procedure, as an orange solid (13%). ¹H NMR (CDCl₃): δ 9.01 (br s, 1H NH), 6.06 (m, 1H, CH=CH₂), 5.47 (m, 2H, CH=CH₂), 4.64–4.52 (m, 6H, NCH₂, subst Cp), 4.21 (s, 5H, Cp). ¹³C{¹H} NMR (CDCl₃): δ 261.6 (C=CMo), 213.3 (MoCO), 206.7 (MoCO), 132.2 (CH=CH₂), 119.9 (CH=CH₂), 95.6 (C_{ipso}, fc), 71.1 (CH, subst Cp), 70.1 (Cp), 56.9 (NCH₂). IR (KBr): ν/cm⁻¹

3316 (NH), 2059 (CO), 1903 (CO), 1869 (CO). MS (FAB⁺): *m/z* 489 (M⁺). HR-MS (FAB⁺) C₁₉H₁₅FeMoNO₅: Calc. 490.9354. Found: 490.9371%.

[(η²-*Allylamino*)(ferrocenyl)methylidene]pentacarbonylchromium(0) **9a**: To a solution of **8a** (0.5 g, 1.12 mmol) in benzene (30 ml) was added at room temperature 0.1 ml of allylamine (1.3 mmol), then the reaction was stirred at reflux for overnight. The solvent was evaporated under vacuum and then the product was purified by chromatography on silicagel using hexane–ethylacetate (4:1) as the eluent to give 0.45 g of an orange solid (96%). ¹H NMR (CDCl₃): δ 8.19 (s, 1H NH), 4.86 (s, 1H, subst Cp), 4.70 (m, 1H, CH=CH₂), 4.60 (s, 1H, subst Cp), 4.53 (s, 1H, subst Cp), 4.46 (s, 1H, subst Cp), 4.26 (s, 5H, Cp), 4.19 (m, 2H, NCH₂), 3.14 (m, 1H, CH=CH₂), 2.88 (m, 1H, CH=CH₂). ¹³C{¹H} NMR (CDCl₃): δ 275.1 (C=Cr), 234.7 (CrCO), 226.9 (CrCO), 226.2 (CrCO), 85.7 (C_{ipso}, fc), 76.0 (CH, subst Cp), 74.0 (CH, subst Cp), 73.1 (CH, subst Cp), 72.1 (CH, subst Cp), 70.0 (Cp), 64.2 (CH=CH₂), 63.4 (CH=CH₂), 52.6 (NCH₂). IR (KBr): ν/cm⁻¹ 3332 (NH), 2006 (CO), 1906 (CO), 1848 (CO). MS (FAB⁺): *m/z* 417 (M⁺), 361 (M⁺ – 2CO), 333 (M⁺ – 3CO). HR-MS (FAB⁺) C₁₈H₁₅CrFeNO₄: Calc. 416.9756. Found: 416.9765%.

[(η²-*Allylamino*)(ferrocenyl)methylidene]pentacarbonylmolybdenum(0) **9c**: A solution of **2c** (0.5 g, 1.12 mmol) (30 ml) was stirred at reflux for overnight and then the solvent was eliminated under vacuum. The product was purified by chromatography on silicagel using hexane–ethylacetate (7:3) as the eluent to give 0.45 g of an orange solid (86%). ¹H NMR (CDCl₃): δ 8.41 (s, 1H NH), 4.86 (s, 1H, subst Cp), 4.70 (m, 1H, CH=CH₂), 4.60 (s, 1H, subst Cp), 4.53 (s, 1H, subst Cp), 4.46 (s, 1H, subst Cp), 4.20 (s, 5H, Cp), 4.03 (m, 2H, NCH₂), 3.49 (m, 1H, CH=CH₂), 2.88 (m, 1H, CH=CH₂). ¹³C{¹H} NMR (CDCl₃): δ 264.1 (C=Mo), 219.7 (MoCO), 210.9 (MoCO), 208.2 (MoCO), 95.6 (C_{ipso}, fc), 76.0 (CH, subst Cp), 74.0 (CH, subst Cp), 73.1 (CH, subst Cp), 72.1 (CH, subst Cp), 70.0 (Cp), 64.2 (CH=CH₂), 63.4 (CH=CH₂), 52.6 (NCH₂). IR (KBr): ν/cm⁻¹ 3332 (NH), 2006 (CO), 1906 (CO), 1848 (CO). MS (FAB⁺): *m/z* 463 (M⁺), 407 (M⁺ – 2CO), 379 (M⁺ – 3CO). HR-MS (FAB⁺) C₁₈H₁₅FeMoNO₄: Calc. 462.9404. Found: 462.9457%.

[(*N*-Methyl-allylamino)(ferrocenyl)methylidene]pentacarbonyltungsten(0) **10**: To a solution of **9b** (0.5 g, 1.19 mmol) in anhydrous THF (20 ml) was added at 0 °C 0.7 mL of a 1.7 M solution of *t*-butyllithium in pentane (1.19 mmol), the mixture was stirred 15 min at this temperature then allowed to warm at room temperature. A solution of CH₃I (0.1 ml, 1.6 mmol) was added by canula and then the solution was stirred 2 h at room temperature. The solvent was removed under vacuum; the mixture was purified by chromatography on silicagel using hexane as eluent to give 0.45 g of a brown solid

(90%). ^1H NMR (CDCl_3): δ 5.98 (m, 1H, $\text{CH}=\text{CH}_2$), 5.51 (m, 2H, $\text{CH}=\text{CH}_2$), 4.55–4.46 (m, 6H, NCH_2 , subst Cp), 4.21 (s, 5H, Cp), 3.96 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 251.9 ($\text{C}=\text{CW}$), 204.3 (WCO), 199.1 (WCO), 132.1 ($\text{CH}=\text{CH}_2$), 120.0 ($\text{CH}=\text{CH}_2$), 96.4 (C_{ipso} , fc), 72.2 (CH, subst Cp), 70.1 (CH, subst Cp), 69.9 (Cp), 59.3 (NCH_2), 42.1 (CH_3). IR (KBr): ν/cm^{-1} 2059 (CO), 1903 (CO), 1869 (CO). MS (FAB^+): m/z 591 (M^+), 507 ($\text{M}^+ - 3\text{CO}$), 479 ($\text{M}^+ - 4\text{CO}$). HR-MS (FAB^+) $\text{C}_{20}\text{H}_{17}\text{FeNO}_5\text{W}$: Calc. 590.9966. Found: 590.9979%.

[(N-Methyl- η^2 -Allylamino)(ferrocenyl)methylidene]pentacarbonylchromium(0) 11a: To a solution of **3a** (0.5 g, 1.19 mmol) in anhydrous THF (20 ml) was added at 0 °C 0.6 mL of a 2.0 M solution of LDA in THF (1.19 mmol), the mixture was stirred 15 min at this temperature then allowed to warm at room temperature. A solution of CH_3I (0.1 ml, 1.6 mmol) was added by canula and then the solution was stirred 2 h at room temperature. The solvent was removed under vacuum; the mixture was purified by chromatography on silicagel using hexane as eluent to give 0.45 g of a brown solid (85%). ^1H NMR (CDCl_3): δ 4.70 (s, 1H, subst Cp), 4.51 (s, 1H, subst Cp), 4.45–4.30 (m, 3H, $\text{CH}=\text{CH}_2$ and subst Cp), 4.46 (s, 1H, subst Cp), 4.17 (m, 2H, NCH_2), 4.11 (s, 5H, Cp), 3.51 (s, 3H, CH_3), 3.07 (d, 1H, $J = 9$ Hz, $\text{CH}=\text{CH}_2$), 2.93 (d, 1H, $J = 13$ Hz,

$\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 274.7 ($\text{C}=\text{Cr}$), 234.0 (CrCO), 228.0 (CrCO), 226.3 (CrCO), 226.0 (CrCO), 85.6 (C_{ipso} , fc), 73.6 (CH, subst Cp), 73.5 (CH, subst Cp), 72.0 (CH, subst Cp), 72.5 (CH, subst Cp), 70.5 ($\text{CH}=\text{CH}_2$), 69.5 (Cp), 66.2 (NCH_2), 63.5 ($\text{CH}=\text{CH}_2$), 42.8 (CH_3). IR (KBr): ν/cm^{-1} 2003 (CO), 1901 (CO), 1838 (CO). MS (FAB^+): m/z 431 (M^+), 375 ($\text{M}^+ - 2\text{CO}$), 347 ($\text{M}^+ - 3\text{CO}$), 319 ($\text{M}^+ - 4\text{CO}$). HR-MS (FAB^+) $\text{C}_{19}\text{H}_{17}\text{CrFeNO}_4$: Calc. 430.9912. Found: 430.9926%.

[(N-Methyl- η^2 -Allylamino)(ferrocenyl)methylidene]pentacarbonylmolibdenum(0) 11c: The complex **11c** was obtained by a similar procedure, as an orange solid (82%). ^1H NMR (CDCl_3): δ 4.86 (s, 1H, subst Cp), 4.70 (m, 1H, $\text{CH}=\text{CH}_2$), 4.60 (s, 1H, subst Cp), 4.53 (s, 1H, subst Cp), 4.46 (s, 1H, subst Cp), 4.20 (s, 5H, Cp), 4.03 (m, 2H, NCH_2), 3.68 (s, 3H, CH_3), 3.49 (m, 1H, $\text{CH}=\text{CH}_2$), 2.88 (m, 1H, $\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 264.1 ($\text{C}=\text{Mo}$), 219.7 (MoCO), 210.9 (MoCO), 208.2 (MoCO), 95.6 (C_{ipso} , fc), 76.0 (CH, subst Cp), 74.0 (CH, subst Cp), 73.1 (CH, subst Cp), 72.1 (CH, subst Cp), 70.0 (Cp), 64.2 ($\text{CH}=\text{CH}_2$), 63.4 ($\text{CH}=\text{CH}_2$), 52.6 (NCH_2), 45.3 (CH_3). IR (KBr): ν/cm^{-1} 2006 (CO), 1906 (CO), 1848 (CO). MS (FAB^+): m/z 477 (M^+), 421 ($\text{M}^+ - 2\text{CO}$), 393 ($\text{M}^+ - 3\text{CO}$). HR-MS (FAB^+) $\text{C}_{19}\text{H}_{17}\text{FeMoNO}_4$: Calc. 476.9561. Found: 476.9575%.

Table 5
Crystal data and structure refinement for **3a**, **3b**, **9a** and **11a**

	3a	3b	9a	11a
Formula	$\text{C}_{18}\text{H}_{14}\text{CrFeO}_6$	$\text{C}_{18}\text{H}_{14}\text{FeNO}_6\text{W}$	$\text{C}_{18}\text{H}_{15}\text{CrFeNO}_4$	$\text{C}_{19}\text{H}_{17}\text{CrFeNO}_4$
Formula weight (g mol^{-1})	434.14	565.99	417.16	431.19
Crystal size (mm)	$0.270 \times 0.262 \times 0.262$	$0.298 \times 0.164 \times 0.116$	$0.264 \times 0.164 \times 0.034$	$0.156 \times 0.138 \times 0.136$
Color	Deep-red	Deep-red	Orange	Red
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	7.4013(3)	7.3484(4)	7.101(1)	16.941(1)
<i>b</i> (Å)	13.551(1)	13.681(1)	13.059(1)	8.422(1)
<i>c</i> (Å)	17.921(1)	18.231(1)	18.383(1)	13.671(1)
α (°)	90	90	90	90
β (°)	90	90	96.861(2)	113.055(1)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	1797.4(2)	1832.8(2)	1692.5(3)	1794.7(3)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (g cm^{-3})	1.604	2.051	1.637	1.596
No. of collected reflections	24932	17620	23082	24237
No. of independent reflections (R_{int})	6477 unique (0.0484)	6501 unique (0.0538)	6120 unique (0.0702)	6488 unique (0.0679)
Absorption correction method	Analytical: face-indexes	Analytical: face-indexes	Analytical: face-indexes	Analytical: face-indexes
Maximum and minimum transmission	0.7588 and 0.6841	0.4752 and 0.1915	0.9454 and 0.7041	0.4752 and 0.1915
Data/parameters	6477/291	6501/236	6120/229	6488/248
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0398$, $wR_2 = 0.0580$	$R_1 = 0.0382$, $wR_2 = 0.0490$	$R_1 = 0.0522$, $wR_2 = 0.0572$	$R_1 = 0.0449$, $wR_2 = 0.0779$
<i>R</i> indices (all data)	$R_1 = 0.0604$, $wR_2 = 0.0619$	$R_1 = 0.0659$, $wR_2 = 0.0534$	$R_1 = 0.1290$, $wR_2 = 0.0635$	$R_1 = 0.1025$, $wR_2 = 0.1141$
Goodness-of-fit on F^2	0.995	0.995	0.999	1.006

3.5. X-ray crystal structure determinations for complex **3a**, **3b**, **9a** and **11b**

Data collection and refinement parameters are summarized in Table 5. The diffraction data were collected on a Bruker Smart Apex CCD diffractometer with Mo K α radiation, $\lambda = 0.71063 \text{ \AA}$. Each data set was corrected for Lorentz and polarization effects and empirical absorption corrections based on ψ -scans were applied. The structures were solved by direct methods [4] and each structure was refined by full-matrix least-squares on F^2 using all data with the all non-hydrogen atoms assigned anisotropic displacement parameters and hydrogen atoms bound to carbon atoms inserted at calculated position with isotropic temperature factor 1.2 times the Uiso of the parent carbon atom. The program used in the final refinements was SHELXL-97 [5]. Selected bond lengths and bond angles are shown in Tables 1–4.

4. Supplementary data

Crystallographic data or the structural analysis has been deposited with the Cambridge Crystallographic Centre CCDC No. 262965 for complex **3a**, No. 262966 for complex **3b**, No. 262967 for complex **9a**, and No. 262968 for complex **11a**. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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