

Nucleophilic addition of chromium and tungsten carbene anions to cationic organotricarbonylmetallic complexes

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Abstract

Anions formed by deprotonation of alkoxy and amino Fischer carbene complexes of chromium and tungsten have been used as nucleophiles with η^6 and η^5 organotricarbonylmetal complexes of manganese and iron to form bimetallic organo-linked products, of which one has been studied by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Chromium carbene; Tungsten carbene; η^6 -Arene; η^5 -Cyclohexadienyl; Manganese complexes; Iron complexes

1. Introduction

It is well established that hydrogen atoms α to the carbene carbon atom in 'Fischer type' carbene complexes can be easily removed upon treatment with bases [1] to form carbene anions or carbene 'enolates' which possess in some aspects a chemistry similar to that of ketone or ester enolates [2]. These carbene anions have been found to add to cationic Re, Cr and Mo complexes [3] as well as to cationic Fe cyclohexadienyl complexes [4].

It is also well known that cationic tricarbonylmanganese complexes of arenes can be easily attacked by nucleophiles such as ketone enolates and ester enolates [5–13], and cyclohexadienyliron complexes show similar reactivity with stabilised enolates.

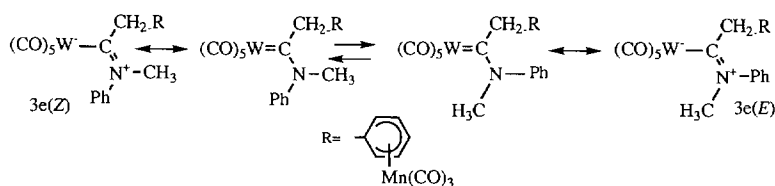
In the course of our studies aimed at the reactivity of these cationic organotricarbonylmetal complexes [14], we considered the possibility of adding metallo carbene anions to these very electrophilic arene complexes [15].

Herein we report the full details of the syntheses of five new η^5 -cyclohexadienyl complexes resulting from the addition of anionic Fischer type carbenes of W and Cr to the (η^6 -benzene)tricarbonylmanganese cation, the X-ray analysis of one of them, and the extension of the methodology to the use of substituted η^5 -tricarbonyliron cations.

2. Results and discussion

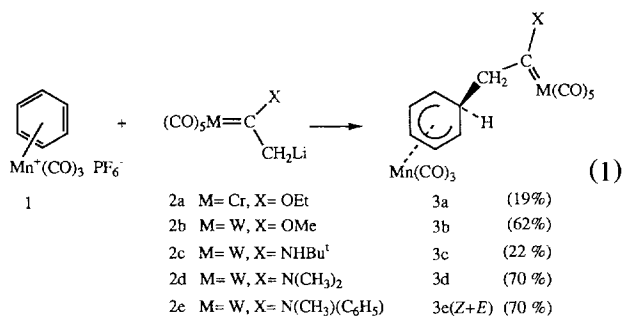
The lithiated complexes of **2a–2e** were found to attack very easily at low temperature with cationic com-

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Scheme 1.

plex **1** to yield the corresponding η^5 -cyclohexadienyl complexes **3a–3e** (Eq. (1)).

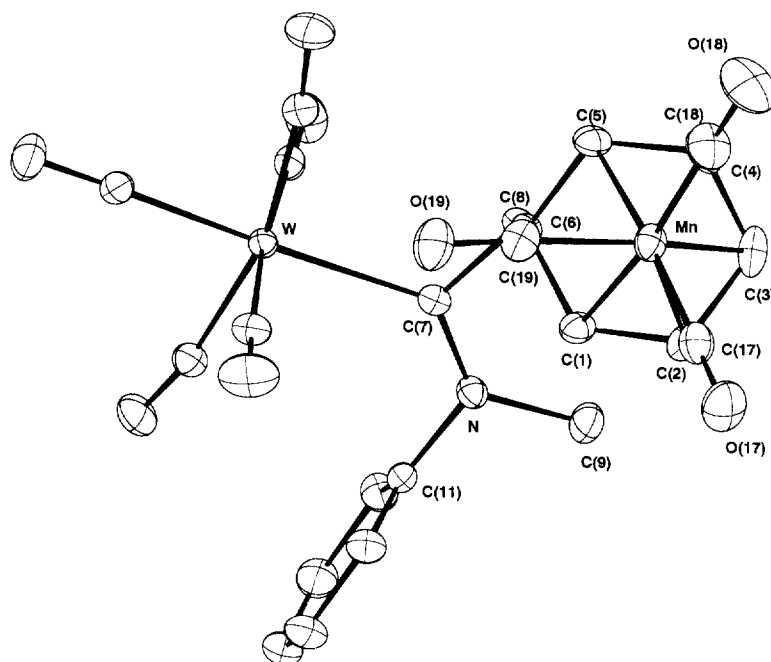


Deprotonation of **2c** at nitrogen to give $[(\text{CO})_5\text{W}-\text{C}(=\text{NBu}^t)\text{CH}_3]^-$ was favored over deprotonation at carbon to give $[(\text{CO})_5\text{W}-\text{C}(\text{NHBu}^t)=\text{CH}_2]^-$. The two anions may be in equilibrium and the minor isomer (the carbanion) may react to give **3c** in low yield (22%). The best yields were obtained with carbene tungsten complexes, the stabilizing heteroatom being either an oxygen atom (62% for **3b**) or saturated nitrogen (70% for **3d**). In the five new complexes **3a–3e**, the IR spectra indicate the presence of $\text{M}(\text{CO})_5$ and $\text{M}(\text{CO})_3$ units, ¹H

and ¹³C data given in Section 3 are consistent with an η^5 -cyclohexadienyl structure for Mn complex **3**. In the case of complex **3e**, two stereoisomers were formed and separated by column chromatography. Indeed, it is known [16] that such aminocarbene complexes exist as a mixture of two isomers differing in orientation around the C–N partial double bond (Scheme 1).

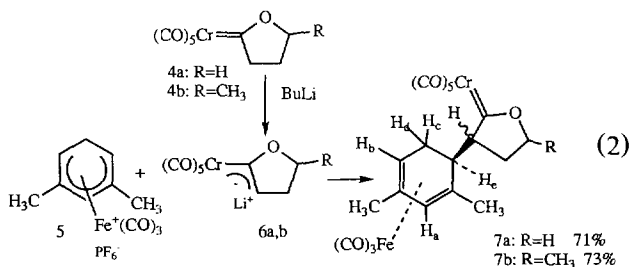
In one case, we were able to obtain crystals of one of the **3e** stereoisomers, suitable for an X-ray study. The ORTEP view (Fig. 1) clearly shows that the preferred structure is the Z isomer: **3e(Z)** with the phenyl group *cis* to the $\text{W}(\text{CO})_5$ entity.

Five ring carbon atoms (C1, C2, C3, C4, C5) are almost coplanar, while the remaining atom C6 lies on the opposite side of this plane from the $\text{Mn}(\text{CO})_3$ moiety. The plane makes an angle of 38° with that defined by C1, C6 and C5. As expected the sp³ carbon atom in the ring is eclipsed by an Mn–CO bond [11–13,17]. The C8–N carbon nitrogen bond length (1.327 Å) and W–C8 bond length (2.260 Å) are in good agreement with literature data of mononuclear aminocarbene complexes [18], so the presence of another metallic atom (Mn) in the molecule does not seem to affect the carbenic structure.

Fig. 1. ORTEP view of **3e(Z)**.

In the ^1H NMR spectra of amino carbene complexes of chromium a downfield shift for the hydrogen atoms of *Z* alkyl substituents of the nitrogen is generally observed [19]. In the case of complex **3e**, a reversed situation was observed in that the methyl group of isomer **3e(E)** resonates at 4.0 ppm, while it is at 3.58 ppm in isomer **3e(Z)**. This is attributed to the shielding effect of the η^5 -cyclohexadienyl entity.

Since cyclic Fischer carbene complexes such as **4** are synthetic equivalents of the biologically important γ -butyrolactones [20] and Δ^2 -dihydrofurans [21], it seemed to us interesting to examine the reactivity of the conjugate base **6a,b** of the pentacarbonyl(2-oxacyclohexylidene)chromium(0) complexes **4a,b** towards the tricarbonyliron(η^5 -cyclohexadiene) cation complex **5** used as electrophile. The reaction was initially kept at -78°C , and then gradually warmed to room temperature to obtain a good conversion of the starting reagents. After quenching the reaction with water, the expected neutral hetero-bimetallic complexes **7a,b** were obtained in good chemical yields (71 and 73% respectively) as stereoisomeric mixtures (Eq. (2)).



In the case of complex **7a**, a 9:1 ratio between the two expected diastereoisomers has been determined from the areas of the vinylic H_a hydrogen signals of the iron-complexed cyclohexadiene portion which resonate at 5.22 ppm (major diastereoisomer) and 5.28 ppm (minor one) in the ^1H NMR spectrum of the crude reaction mixture. Attempts to separate the two diastereoisomers by conventional chromatographic techniques were unsuccessful, but the major diastereoisomer was obtained analytically pure by repeated crystallizations from pentane. The presence of a stereogenic center on the carbene complex **4b** results in a more complicated analysis of the diastereoisomeric mixture of the corresponding complex **7b**. In this case the ^1H NMR of the crude reaction mixture showed the presence of three of the four possible diastereoisomers. A ratio of 7:1:1 between them has been estimated from the areas of the methynic H_e hydrogen signals of the iron complexed cyclohexadiene, observed at 3.42, 3.55 and 3.15 ppm respectively, which fall in a clear part of the spectrum.

Based only on the spectroscopic data, it is not possible to assign the relative stereochemistry of the newly formed stereocenters present in **7**. However, some infer-

ences may be drawn from the following points. (i) The $\text{Fe}(\text{CO})_3$ group shields one side of the complex **5** so the nucleophilic addition of the conjugated base **6** must occur on the opposite side. As a result of this, the hydrogen bound to the carbon atom that undergoes the nucleophilic attack should be found on the same side of the $\text{Fe}(\text{CO})_3$ group in **7**. (ii) A similar acidity is expected for the α -carbene hydrogens of both the starting complexes **4a,b** and their addition products **7a,b**. Thus it is anticipated that under the reaction conditions, an equilibrium between their conjugate bases should exist. This could account for the long reaction times and high temperatures required. In addition, the formation of the conjugate base of **7** should influence the observed diastereoisomeric ratios depending on of the thermodynamic stabilities of each of the diastereoisomers.

In conclusion, addition of chromium and tungsten carbene carbanions to cationic (η^6 -benzene)tricarbonylmanganese gives new neutral heterodinuclear complexes, of which one has been fully characterized by X-ray analysis. In the course of this work the combination of a prochiral organometallic electrophile and a chiral racemic chromium alkoxycarbene complex has been found to show significant diastereoselectivity. Efficient nucleophile addition reactions are possible and could provide a synthetically valuable procedure for the formation of bimetallic compounds which in turn might be useful in probing chemical reactions between two different metal centers which are not directly bonded to each other.

3. Experimental

3.1. General

The carbene complexes $(\text{CO})_5\text{Cr}=\text{C}(\text{OC}_2\text{H}_5)(\text{CH}_3)$ **2a** [22], $(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)(\text{CH}_3)$ **2b** [22], $(\text{CO})_5\text{W}=\text{C}(\text{NHBU}^t)(\text{CH}_3)$ **2c** [23], $(\text{CO})_5\text{W}=\text{C}[\text{N}(\text{CH}_3)_2](\text{CH}_3)$ **2d** [24], $(\text{CO})_5\text{W}=\text{C}[\text{NH}(\text{C}_6\text{H}_5)](\text{CH}_3)$ **2e** [25] were prepared by literature procedures. Complexes **4** were prepared as reported in Ref. [20]. The reagent *n*-BuLi (1.6 M solution in hexane) was purchased from Aldrich Chemical Co. and used as received. THF was dried by refluxing over Na/benzophenone ketyl. DMF was dried by filtering over a neutral Al_2O_3 pad just before use. All manipulations were performed using a vacuum line under an N_2 atmosphere. IR spectra were recorded on a Perkin-Elmer 1420 (Paris) or a Perkin-Elmer 298 spectrophotometer (Milan). NMR spectra were obtained using a Bruker AC200 and Jeol GSX400 (Paris) or Varian XL-300 and Gemini 200 MHz (Milan) NMR spectrometer. Elemental analyses were obtained from the Service de Microanalyse de l'Université P. et M. Curie, Paris, France.

3.2. Preparation of $(CO)_5W=C[N(CH_3)(C_6H_5)](CH_3)$ **2e**

The same method as that described for the preparation of $(CO)_5W=C[N(CH_3)_2](CH_3)$ [24] was used. To a THF solution of $(CO)_5W=C[NH(C_6H_5)](CH_3)$ (2.88 g, 6.51 mmol) at -60°C was added lithium diisopropylamide (6.60 mmol). After stirring for 30 min, MeI (530 ml, 8.51 mmol) was added. After extraction with ether and evaporation of organic solvents under reduced pressure, the yellow product was purified by silica gel chromatography to give 1.87 g (63% yield) of *trans* $(CO)_5W=C[N(CH_3)(C_6H_5)](CH_3)$ obtained with a 4% mixture of ether/ether petroleum as eluent and 0.97 g (33% yield) of the *cis* complex obtained with a 60% mixture of ether/petroleum ether as eluent.

Trans complex Anal. Found: C, 37.16; H, 2.46; N, 3.15. $C_{14}H_{11}NO_5W$ Calc.: C, 36.79; H, 2.43; N, 3.06%. IR ($CHCl_3$): $\nu(CO)$ 1915, 1965 and 2025 cm^{-1} . ^1H NMR (400 MHz, C_6D_6): δ 2.20 (d, 3H, NCH_3 , $J = 1.1\text{ Hz}$), 3.41 (s, 3H, CH_3), 5.91 (d, 2H of C_6H_5 , $J = 7.7\text{ Hz}$), 6.77 ppm (m, 3H of C_6H_5). ^{13}C NMR (50 MHz, C_6D_6): δ 44.1 (NCH_3), 55.8 (CH_3), 124.2, 127.6, 130.0 and 145.6 (C_6H_5), 199.5 and 203.5 (W–CO), 258.4 ppm (C=W).

Cis complex Anal. Found: C, 37.15; H, 2.42; N, 3.16. $C_{14}H_{11}NO_5W$ Calc.: C, 36.79; H, 2.43; N, 3.06%. IR ($CHCl_3$): $\nu(CO)$ 1920, 1965 and 2025 cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ 2.27 (s, 3H, NCH_3), 2.28 (s, 3H, CH_3), 6.61 (dd, 2H of C_6H_5 , $J = 8.3$ and 0.9 Hz), 7.02 ppm (m, 3H of C_6H_5). ^{13}C NMR (50 MHz, C_6D_6): δ 42.6 (NCH_3), 43.7 (CH_3), 125.8, 128.8, 130.1 and 152.8 (C_6H_5), 199.4 and 204.4 (W–CO), 260.3 ppm (C=W).

3.3. Addition of **2a** to complex **1** to form complex **3a**

In a typical procedure, to a THF solution (10 ml) of chromium carbene anion **2a** (201.6 mg, 0.76 mmol) at -78°C under N_2 was added *n*-BuLi (525 ml of a 1.6 M solution in hexanes, 0.84 mmol). After 5 min, the resulting solution was transferred by cannula to a second flask containing a suspension of complex **1** (296.4 mg, 0.76 mmol) in THF (5 ml) at -78°C . After 3 min, ether (30 ml) and water (20 ml) were introduced into the flask. After extraction with ether, the organic phase was washed with saturated aqueous NaCl and dried over $MgSO_4$. After evaporation of the organic solvents under reduced pressure, a crude oil was obtained which was purified by silica gel chromatography (petroleum ether) giving **3a** (70.2 mg, 19% yield).

Complex **3a** Anal. Found: C, 45.18; H, 2.75. $C_{18}H_{13}CrMnO_9$ Calc.: C, 45.02; H, 2.73%. IR (CCl_4): $\nu(CO, Cr)$ 1940 and 2025; $\nu(CO, Mn)$ 1940 and 2005 cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ 0.88 (t, 3H, CH_3 , $J = 7.0\text{ Hz}$), 2.34 (m, 2H, CH_2), 2.38 (m, 2H, H1

and H5), 2.61 (m, 1H, H6), 4.04 (t, 2H, H2 and H4, $J = 5.7\text{ Hz}$), 4.44 (quadr, 2H, OCH_2 , $J = 7.0\text{ Hz}$), 4.93 ppm (t, 1H, H3, $J = 5.7\text{ Hz}$). ^{13}C NMR (100 MHz, C_6D_6): δ 14.7 (CH_3), 33.3 (C6), 56.0 (C1 and C5), 75.5 (CH_2), 78.2 (OCH_2), 80.2 (C3), 96.6 (C2 and C4), 216.9 and 223.8 (Cr–CO), 223.2 (Mn–CO), 357.4 ppm (C=Cr).

3.4. Addition of **2b** to complex **1** to form complex **3b**

This compound was prepared similarly to **3a** using **2b** (383.2 mg, 1 mmol), *n*-BuLi (687 ml, 1.1 mmol) and **1** (361.5 mg, 1 mmol). Chromatography and isolation as above for **3a** gave **3b** as a yellow solid (368.9 mg, 62% yield).

Complex **3b** Anal. Found: C, 34.06; H, 1.83. $C_{17}H_{11}MnO_9W$ Calc.: C, 34.14; H, 1.85%. IR (CCl_4): $\nu(CO, W)$ 1940, 1975 and 2030; $\nu(CO, Mn)$ 1940 and 2005 cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ 2.16 (d, 2H, CH_2 , $J = 6.6\text{ Hz}$), 2.34 (t, 2H, H1 and H5, $J = 5.6\text{ Hz}$), 2.59 (m, 1H, H6), 3.67 (s, 3H, OCH_3), 4.04 (t, 2H, H2 and H4, $J = 5.6\text{ Hz}$), 4.93 ppm (tt, 1H, H3, $J = 5.6$ and 1.3 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 33.1 (C6), 55.7 (C1 and C5), 69.8 (OCH_3), 76.8 (CH_2), 79.9 (C3), 96.4 (C2 and C4), 197.3 and 203.4 (W–CO), 222.9 (Mn–CO), 333.4 ppm (C=W).

3.5. Addition of **2c** to complex **1** to form complex **3c**

This compound was prepared similarly to **3a** using **2c** (422 mg, 1 mmol), *n*-BuLi (687 ml, 1.1 mmol) and **1** (362 mg, 1 mmol). Chromatography and isolation as above for **3a** gave **3c** as a yellow solid (137.5 mg, 22% yield).

Complex **3c** Anal. Found: C, 37.79; H, 2.89; N, 2.14. $C_{20}H_{18}MnNO_8W$ Calc.: C, 37.58; H, 2.84; N, 2.19%. IR ($CHCl_3$): $\nu(CO, W)$ 1925 and 2055; $\nu(CO, Mn)$ 1925 and 2010 cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ 0.59 (s, 9H, Bu^t), 1.79 (d, 2H, CH_2 , $J = 7.1\text{ Hz}$), 2.67 (t, 2H, H1 and H5, $J = 5.8\text{ Hz}$), 3.51 (m, 1H, H6), 4.04 (t, 2H, H2 and H4, $J = 5.8\text{ Hz}$), 4.85 (t, 1H, H3, $J = 5.8\text{ Hz}$), 8.51 ppm (s, 1H, NH). ^{13}C NMR (100 MHz, C_6D_6): δ 30.4 (CH_3 of Bu^t), 37.7 (C6), 56.4 (C1 and C5), 60.0 (C of Bu^t), 60.7 (CH_2), 78.8 (C3), 96.7 (C2 and C4), 199.8 and 203.2 (CO, W), 222.8 (CO, Mn), 260.0 ppm (C=W).

3.6. Addition of **2d** to complex **1** to form complex **3d**

This compound was prepared similarly to **3a** using **2d** (395 mg, 1 mmol), *n*-BuLi (687 ml, 1.1 mmol) and **1** (363 mg, 1 mmol). Chromatography and isolation as above for **3a** gave **3d** as an orange solid (427.0 mg, 70% yield).

Complex **3d** Anal. Found: C, 35.28; H, 2.32; N, 2.31. $C_{18}H_{14}MnNO_8W$ Calc.: C, 35.38; H, 2.31; N,

2.29%. IR (CHCl₃): $\nu(\text{CO}, \text{W})$ 1920 and 2050; $\nu(\text{CO}, \text{Mn})$ 1920 and 2010 cm⁻¹. ¹H NMR (200 MHz, C₆D₆): δ 1.93 (s, 3H, NCH₃), 2.14 (d, 2H, CH₂, $J = 6.4$ Hz), 2.40 (t, 2H, H1 and H5, $J = 5.7$ Hz), 2.78 (m, 1H, H6), 2.90 (s, 3H, NCH₃), 4.06 (t, 2H, H2 and H4, $J = 5.7$ Hz), 4.92 ppm (t, 1H, H3, $J = 5.7$ Hz). ¹³C NMR (50 MHz, C₆D₆): δ 33.7 (C6), 41.5 (NCH₃), 55.5 (NCH₃), 56.1 (C1 and C5), 65.9 (CH₂), 79.6 (C3), 96.4 (C2 and C4), 199.4 and 202.6 (CO, W), 222.6 (CO, Mn), 254.8 ppm (C=W).

3.7. Addition of 2e to complex 1 to form complex 3e(E + Z)

This compound was prepared similarly to 3a using 2e (457.5 mg, 1 mmol), n-BuLi (687 ml, 1.1 mmol) and 1 (362 mg, 1 mmol). Chromatography and isolation as above for 3a gave 3e(E) as a yellow solid (211.4 mg, 32% yield) and 3e(Z) as a yellow solid (261.1 mg, 39% yield).

Complex 3e(E) Anal. Found: C, 41.10; H, 2.50; N, 2.12. C₂₃H₁₆MnNO₈W Calc.: C, 41.04; H, 2.40; N, 2.08%. IR (CHCl₃): $\nu(\text{CO}, \text{W})$ 1915, 1960 and 2050; $\nu(\text{CO}, \text{Mn})$ 1915 and 2010 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 2.40 (d, 2H, CH₂, $J = 6.3$ Hz), 3.00 (t, 2H, H1 and H5, $J = 6.0$ Hz), 3.25 (m, 1H, H6), 4.00 (s, 3H, NCH₃), 4.62 (t, 2H, H2 and H4, $J = 6.0$ Hz), 5.47 (tt, 1H, H3, $J = 6.0$ and 1.2 Hz), 7.01 (m, 2H of C₆H₅), 7.46 ppm (m, 3H of C₆H₅). ¹³C NMR (50 MHz, CDCl₃): δ 35.7 (C6), 56.2 (C1 and C5), 57.6 (NCH₃), 67.5 (CH₂), 79.6 (C3), 96.4 (C2 and C4), 125.7, 128.8, 130.1 and 152.7 (C₆H₅), 198.8 and 202.6 (CO, W), 222.3 (CO, Mn), 260.8 ppm (C=W).

Complex 3e(Z) Anal. Found: C, 41.05; H, 2.41; N, 2.04. C₂₃H₁₆MnNO₈W Calc.: C, 41.04; H, 2.40; N, 2.08%. IR (CHCl₃): $\nu(\text{CO}, \text{W})$ 1920, 1950 and 2050; $\nu(\text{CO}, \text{Mn})$ 1920 and 2015 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 2.92 (d, 2H, CH₂, $J = 6.5$ Hz), 3.31 (t, 2H, H1 and H5, $J = 5.8$ Hz), 3.49 (m, 1H, H6), 3.58 (s, 3H, NCH₃), 4.96 (t, 2H, H2 and H4, $J = 5.8$ Hz), 5.88 (tt, 1H, H3, $J = 5.8$ and 1.2 Hz), 7.13 (m, 2H of C₆H₅), 7.44 ppm (m, 3H of C₆H₅). ¹³C NMR (50 MHz, CDCl₃): δ 35.3 (C6), 46.1 (NCH₃), 56.0 (C1 and C5), 66.1 (CH₂), 80.0 (C3), 97.0 (C2 and C4), 125.4, 129.1, 130.6 and 153.4 (C₆H₅), 198.8 and 203.5 (CO, W), 222.1 (CO, Mn), 261.3 ppm (C=W).

3.8. General procedure for the synthesis of the complexes 7

To a dry THF solution of the conjugate base of the pentacarbonyl(2-oxacyclopentylidene)chromium(0) 6a,b [generated by treatment of the corresponding carbene complexes 4a,b (250 mg, 0.9 mmol) with n-BuLi 1.6 M hexane solution (0.9 mmol, 0.62 ml) in THF (25 ml) at -78°C, 20 min] the iron-dienyl cation 5 (355 mg, 0.9 mmol) was added at -78°C. The resulting orange

reaction mixture was kept at -78°C for 30 min, at -60°C for 45 min and then overnight at room temperature. The solvent was evaporated at reduced pressure and the crude reaction mixture taken up with water and extracted with CH₂Cl₂ (2 × 100 ml). The organic layer was then washed with water, dried over Na₂SO₄ and the solvent removed under reduced pressure. The crude reaction products were purified by flash chromatography.

Complex 7a: with light petroleum/CH₂Cl₂ (9:1) as eluent, 64 mg (0.24 mmol) of the unreacted starting complex 4a was recovered. With light petroleum/CH₂Cl₂ (1:1), 325 mg (0.64 mmol, 71% and 94% on converted 4a) of the complex 7a was obtained as a diastereoisomeric mixture.

After two crystallizations from pentane, the pure major diastereoisomer was obtained as a yellow solid.

Data for the major diastereoisomer: m.p. 99°C (pentane). IR (Nujol): $\nu(\text{CO}, \text{Cr})$ 2064; $\nu(\text{CO}, \text{Fe})$ 2040; $\nu(\text{CO}, \text{Cr}, \text{Fe})$ broad band 1990–1870 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 5.22 (s, 1H, C=CH-C), 4.92–4.72 (m, 2H, =C-O-CH₂), 3.72 (ddd, 1H, $J_{\text{vic1}} = 9.9$ Hz, $J_{\text{vic2}} = 6.7$ Hz, $J_{\text{vic3}} = 3.3$ Hz, Cr=C-CH), 3.51 (ddd, $J_{\text{vic1}} = 10.7$ Hz, $J_{\text{vic2}} = J_{\text{vic3}} = 3.3$ Hz, =C-CH-CH₂-CH=), 2.90 (broad s, 1H, =C-CH-CH₂-CH=), 2.16 (ddd, 1H, $J_{\text{gem}} = 15.4$ Hz, $J_{\text{vic1}} = 10.7$ Hz, $J_{\text{vic2}} = 3.6$ Hz, -C-CH-C(H)-CH=), 2.03 (s, 3H, CH=C(CH₃)-CH=), 1.83 (m, 1H, Cr=C-CH-C(H)-H-), 1.69 (s, 3H, CH-(CH₃)C=CH), 1.30 (m, 1H, Cr=C-CH-C(H)-H-), 0.73 ppm (ddd, 1H, $J_{\text{gem}} = 15.4$ Hz, $J_{\text{vic1}} = 10.7$ Hz, $J_{\text{vic2}} = 3.6$ Hz, =C-CH-C(H)-H-CH=). ¹³C NMR (300 MHz, CDCl₃): δ 346.02 (C_{carbene}), 222.83 (CO_{trans}, Cr(CO)₅), 216.41 (CO_{cis}, Cr(CO)₅), 211.68 (CO, Fe(CO)₃), 98.67 (C_{quat}), 89.19 (=CH-), 85.54 (O-CH₂-), 73.92 (C_{quat}), 73.14 (=CH-), 61.04 (Cr=C-CH-), 44.34 (C=C-CH-CH₂), 28.57 (O-CH₂-CH₂-), 23.47 (CH₃), 21.73 (-CH-CH₂-CH=), 21.65 ppm (CH₃). HRMS (EI): found 505.9545, C₂₀H₁₆O₉FeCr calc. 507.9543. MS (dis) m/z : 508 (3%, M⁺); 480 (1%, M⁺-CO); 452 (2%, M⁺-2CO); 424 (7%, M⁺-3CO); 396 (15%, M⁺-4CO); 368 (30%, M⁺-5CO); 354 (2%, M⁺-6CO); 312 (11%, M⁺-7CO); 284 (33%, M⁺-8CO); 256 (9%, M⁺-9CO); 230 (87%, M⁺-9CO-Fe).

Complex 7b: the first fraction 11 mg (0.04 mmol) collected with light petroleum was the unreacted complex 4b.

With light petroleum/CH₂Cl₂ 9:1, three other fractions were collected; the first one, 192 mg, yellow solid, corresponding to the major diastereoisomer of the complex 7b; the second fraction, 122 mg, yellow solid, was a mixture of the above diastereoisomer and the minor ones; the third fraction, 29 mg, yellow solid, was a mixture of the minor diastereoisomers. Total amount of complex 7b: 343 mg (0.66 mmol, 73% and 77% on the converted 4b).

Data for the major diastereoisomer: m.p. 105–108 °C (pentane). IR (Nujol): $\nu(\text{CO, Cr})$ 2058; $\nu(\text{CO, Fe})$ 2040; $\nu(\text{CO, Cr, Fe})$ broad band 1990–1870 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 5.21 (s, 1H, $\text{C}=\text{CH}-\text{C}=\text{C}$), 5.19 (m, 1H, $\text{Cr}=\text{C}-\text{O}-\text{CH}-\text{CH}_3$), 3.93 (ddd, 1H, $J_{\text{vic}1} = 10$ Hz, $J_{\text{vic}2} = 6$ Hz, $J_{\text{vic}3} = 3$ Hz, $\text{Cr}=\text{C}-\text{CH}-$), 3.42 (dt, 1H, $J_{\text{vic}1} = 9$ Hz, $J_{\text{vic}2} = J_{\text{vic}3} = 3$ Hz, $=\text{C}-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 2.90 (broad s, 1H, $=\text{C}-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 2.08 (ddd, 1H, $J_{\text{gem}} = 15$ Hz, $J_{\text{vic}1} = 10$ Hz, $J_{\text{vic}2} = 3$ Hz, $=\text{C}-\text{CH}-\text{CH}(\text{H})-\text{CH}=\text{C}$), 2.05 (s, 3H, $\text{CH}=\text{C}(\text{CH}_3)-\text{CH}=\text{C}$), 1.65 (s, 3H, $\text{CH}-(\text{CH}_3)\text{C}=\text{CH}-$), 1.43 (d, 3H, $\text{O}-\text{CH}-\text{CH}_3$), 1.51–1.32 (m, 2H, $=\text{C}-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 0.73 ppm (broad t, 1H, $=\text{C}-\text{CH}-\text{CH}(\text{H})-\text{CH}=\text{C}$). ^{13}C NMR (200 MHz, CDCl_3) δ 344.32 ($\text{C}_{\text{carbene}}$), 223.73 (CO_{trans} , $\text{Cr}(\text{CO})_5$), 217.22 (CO_{cis} , $\text{Cr}(\text{CO})_5$), 212.41 (CO , $\text{Fe}(\text{CO})_3$), 99.24 (C_{quat}), 96.70 ($\text{O}-\text{CH}-\text{CH}_3$), 90.05 ($=\text{CH}-$), 74.66 (C_{quat}), 73.84 ($=\text{CH}-$), 61.61 ($\text{Cr}=\text{C}-\text{CH}-$), 45.16 ($\text{C}=\text{C}-\text{CH}-\text{CH}_2$), 29.65 ($\text{O}-\text{CH}-\text{CH}_2$), 28.89 ($-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 24.03 (CH_3), 22.97 (CH_3), 22.35 ppm (CH_3). HRMS (EI): found 521.9771, $\text{C}_{21}\text{H}_{18}\text{O}_9\text{FeCr}$ calc. 521.9705. MS (dis) m/z : 522 (9%, M^+), 494 (3%, $\text{M}^+ - \text{CO}$), 466 (5%, $\text{M}^+ - 2\text{CO}$), 438 (8%, $\text{M}^+ - 3\text{CO}$), 410 (20%, $\text{M}^+ - 4\text{CO}$), 382 (62%, $\text{M}^+ - 5\text{CO}$), 354 (5%, $\text{M}^+ - 6\text{CO}$), 326 (16%, $\text{M}^+ - 7\text{CO}$), 298 (47%, $\text{M}^+ - 8\text{CO}$), 247 (100%, $\text{M}^+ - 8\text{CO}-\text{Cr}$).

Data for one minor diastereoisomer: m.p. 99 °C (pentane). IR (Nujol): $\nu(\text{CO, Cr})$ 2060; $\nu(\text{CO, Fe})$ 2040; $\nu(\text{CO, Cr, Fe})$ broad band 2000–1900 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 5.25 (s, 1H, $\text{C}=\text{CH}-\text{C}=\text{C}$), 5.01 (m, 1H, $\text{Cr}=\text{C}-\text{O}-\text{CH}-\text{CH}_3$), 4.05 (dd, 1H, $J_{\text{vic}1} = 9$ Hz, $J_{\text{vic}2} = 4.5$ Hz, $\text{Cr}=\text{C}-\text{CH}-$), 3.15 (broad t, 1H, $J_{\text{vic}1} = J_{\text{vic}2} = 9$ Hz, $=\text{C}-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 2.85 (broad s, 1H, $=\text{C}-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 2.53 (ddd, 1H, $J_{\text{gem}} = 14$ Hz, $J_{\text{vic}1} = 11$ Hz, $J_{\text{vic}2} = 4.5$ Hz, $=\text{C}-\text{CH}-\text{CH}(\text{H})-\text{CH}=\text{C}$), 2.08 (s, 3H, $\text{CH}=\text{C}(\text{CH}_3)-\text{CH}=\text{C}$), 1.95 (m, 1H, $\text{Cr}=\text{C}-\text{CH}-\text{C}(\text{H})\text{H}-$), 1.67 (d, 3H, $\text{O}-\text{CH}-\text{CH}_3$), 1.45 (m, 1H, $=\text{C}-\text{CH}-\text{C}(\text{H})\text{H}-\text{CH}=\text{C}$), 1.21 (s, 3H, $\text{CH}-(\text{CH}_3)\text{C}=\text{CH}-$), 1.15 ppm (m, 1H, $\text{Cr}=\text{C}-\text{CH}-\text{CH}(\text{H})-$). ^{13}C NMR (200 MHz, CDCl_3): δ 345.92 ($\text{C}_{\text{carbene}}$), 223.62 (CO_{trans} , $\text{Cr}(\text{CO})_5$), 217.55 (CO_{cis} , $\text{Cr}(\text{CO})_5$), 212.35 (CO , $\text{Fe}(\text{CO})_3$), 99.07 (C_{quat}), 95.52 ($\text{O}-\text{CH}-\text{CH}_3$), 92.69 ($=\text{CH}-$), 74.36 (C_{quat}), 71.96 ($=\text{CH}-$), 60.22 ($\text{Cr}=\text{C}-\text{CH}-$), 45.30 ($\text{C}=\text{C}-\text{CH}-\text{CH}_2$), 34.70 ($-\text{CH}-\text{CH}_2-\text{CH}=\text{C}$), 29.66 ($\text{O}-\text{CH}-\text{CH}_2-$), 25.35 (CH_3), 22.27 (CH_3), 21.75 (CH_3). MS (dis) m/z : 522 (10%, M^+), 494 (1%, $\text{M}^+ - \text{CO}$), 466 (5%, $\text{M}^+ - 2\text{CO}$), 438 (10%, $\text{M}^+ - 3\text{CO}$), 410 (15%, $\text{M}^+ - 4\text{CO}$), 382 (100%, $\text{M}^+ - 5\text{CO}$), 354 (7%, $\text{M}^+ - 6\text{CO}$), 326 (14%, $\text{M}^+ - 7\text{CO}$), 298 (40%, $\text{M}^+ - 8\text{CO}$), 247 (60%, $\text{M}^+ - 8\text{CO}-\text{Cr}$).

3.9. X-ray structure of **3e(Z)**

Crystals of **3e(Z)** were grown by slow recrystallization of this complex in ether at -25 °C. Intensity data

were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using Mo K α radiation. Accurate cell dimensions and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well-defined reflections. No decay in the intensities of two standard reflections was observed during the course of data collection. Complete crystal data, collection parameters and other significant details are listed in Table 1. The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using the PC version of CRYSTALS [26]. Scattering factors and corrections for anomalous dispersion were taken from Ref. [27]. The structures were resolved by standard Patterson–Fourier techniques and refined by least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located on a Fourier difference map, and their coordinates were refined with an overall refinable isotropic thermal parameter. The structure was refined to $R = 0.0233$ with the use of 3348 reflections for 357 least-squares parameters. Fractional atomic coordinates are listed in Table 2; selected bond lengths and bond angles are given in

Table 1
Crystal data for $\text{C}_{23}\text{H}_{16}\text{O}_8\text{NMnW}$

F_w	673.2
a (Å)	6.876(2)
b (Å)	17.432(3)
c (Å)	19.995(3)
α (°)	90
β (°)	92.66(2)
γ (°)	90
V (Å ³)	2394(2)
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Linear absorption coefficient μ (cm^{-1})	54.6
Density ρ (g cm^{-3})	1.87
Diffractometer	Enraf–Nonius CAD4
Radiation	Mo K α ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8 + 0.345 \text{tg } \theta$
θ limits (°)	1–25
Temperature of measurement	Room temperature
Octants collected	–8, 8; 0, 18; 0, 20
No. of data collected	4305
No. of unique data collected	4028
No. of unique data used for refinement	3348 (F_o) ² > $3\sigma(F_o)$ ²
R_{int}	0.0197
$R = \sum F_o - F_c / \sum F_o $	0.0232
$R_w = [\sum w(F_o - F_c)^2 / \sum F_o^2]^{1/2}$	0.0253, $w = 1.0$
Absorption correction	DIFABS (min = 0.85, max = 1.19)
Extinction parameter ($\times 10^{-6}$)	93
Goodness of fit s	2.13
No. of variables	357
$\Delta\rho_{\text{min}}$ ($\text{e } \text{Å}^{-3}$)	–0.84
$\Delta\rho_{\text{max}}$ ($\text{e } \text{Å}^{-3}$)	0.64

Table 2
Fractional parameters for C₂₃H₁₆O₈NMnW

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i>
W	0.02143(3)	0.06482(1)	0.22692(1)	0.0332
Mn	0.0342(1)	-0.17549(5)	0.46658(4)	0.0445
C(1)	-0.0239(9)	-0.1597(3)	0.3585(3)	0.0441
C(2)	0.040(1)	-0.2324(4)	0.3731(3)	0.0512
C(3)	0.219(1)	-0.2432(4)	0.4087(3)	0.0559
C(4)	0.322(1)	-0.1780(4)	0.4301(3)	0.0515
C(5)	0.2504(9)	-0.1049(4)	0.4149(3)	0.0450
C(6)	0.1138(8)	-0.0945(3)	0.3540(3)	0.0393
C(7)	0.0872(7)	-0.0621(3)	0.2316(2)	0.0340
C(8)	0.2258(8)	-0.0887(3)	0.2880(3)	0.0395
C(9)	0.077(1)	-0.1995(4)	0.1938(4)	0.0604
C(11)	-0.1270(8)	-0.1032(3)	0.1388(3)	0.0390
C(12)	-0.3194(9)	-0.1042(4)	0.1543(3)	0.0532
C(13)	-0.459(1)	-0.0956(5)	0.1034(5)	0.0666
C(14)	-0.407(1)	-0.0872(4)	0.0386(4)	0.0650
C(15)	-0.215(1)	-0.0855(4)	0.0235(3)	0.0602
C(16)	-0.072(1)	-0.0946(4)	0.0739(3)	0.0512
C(17)	-0.152(1)	-0.2380(4)	0.4940(3)	0.0564
C(18)	0.138(1)	-0.1785(4)	0.5510(3)	0.0663
C(19)	-0.116(1)	-0.0934(4)	0.4776(3)	0.0567
C(20)	-0.2294(9)	0.0431(4)	0.2746(3)	0.0506
C(21)	0.1658(8)	0.0875(3)	0.3157(3)	0.0471
C(22)	-0.0271(8)	0.1758(3)	0.2266(3)	0.0464
C(23)	0.2763(8)	0.0750(3)	0.1814(3)	0.0443
C(24)	-0.1236(8)	0.0702(4)	0.1360(3)	0.0472
O(17)	-0.2732(8)	-0.2767(3)	0.5135(3)	0.0799
O(18)	0.2063(9)	-0.1818(4)	0.6043(3)	0.0923
O(19)	-0.2180(8)	-0.0403(3)	0.4804(3)	0.0812
O(20)	-0.3644(7)	0.0295(4)	0.3023(3)	0.0780
O(21)	0.2449(7)	0.1087(3)	0.3635(2)	0.0700
O(22)	-0.0631(8)	0.2422(3)	0.2267(3)	0.0730
O(23)	0.4203(6)	0.0799(3)	0.1558(3)	0.0679
O(24)	-0.2006(7)	0.0844(3)	0.0859(2)	0.0616
N	0.0191(6)	-0.1177(3)	0.1916(2)	0.0397

Table 3. Complete tables of bond distances, bond angles, hydrogen coordinates, anisotropic thermal parameters, observed and calculated structure factors are available as supplementary material (8 pp.).

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Table 3
Selected interatomic distances (Å) and bond angles (°) for C₂₃H₁₆O₈NMnW

W–C(7)	2.259(5)	Mn–C(1)	2.196(6)
Mn–C(2)	2.117(6)	Mn–C(3)	2.117(7)
Mn–C(4)	2.143(6)	Mn–C(5)	2.222(6)
C(1)–C(2)	1.367(9)	C(1)–C(6)	1.486(8)
C(2)–C(3)	1.41(1)	C(3)–C(4)	1.40(1)
C(4)–C(5)	1.394(9)	C(5)–C(6)	1.513(7)
C(6)–C(8)	1.561(7)	C(7)–C(8)	1.516(7)
C(7)–N	1.327(7)	C(9)–N	1.481(8)
C(11)–N	1.445(6)		
C(2)–C(1)–C(6)	121.6(6)	C(1)–C(2)–C(3)	119.8(6)
C(2)–C(3)–C(4)	117.8(6)	C(3)–C(4)–C(5)	120.4(6)
C(4)–C(5)–C(6)	119.1(6)	C(1)–C(6)–C(5)	103.4(5)
C(1)–C(6)–C(8)	116.2(5)	C(5)–C(6)–C(8)	112.0(5)
C(8)–C(7)–N	114.7(5)	W–C(7)–N	128.7(4)
W–C(7)–C(8)	116.6(4)	C(6)–C(8)–C(7)	109.3(4)
C(7)–N–C(9)	126.7(5)	C(7)–N–C(11)	121.8(4)
C(9)–N–C(11)	111.5(5)		

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