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Hydrocarbon bridged metal complexes: XLII. [1] Addition of aniline tricarbonyl chromium complexes to the dienyl ligands of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$

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Abstract

Aniline tricarbonyl chromium complexes $(\eta^6\text{-}C_6H_4(R)NHR^1)Cr(CO)_3$ ($R = H, CH_3$; $R^1 = H, CH_3$) were used as nucleophiles for addition to $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ to give the heterobimetallic ligand bridged complexes $(OC)_3Cr(\eta^6\text{-}C_6H_4(R)N(R^1)(CH_3)C_5H_5CH_3\text{-}\eta^4)Fe(CO)_3$ and $(OC)_3Cr(\eta^6\text{-}C_6H_4(R)N(R^1)C_5H_6CH_3\text{-}\eta^4)Fe(CO)_3$. The structures of $(OC)_3Cr(\eta^6\text{-}C_6H_4(CH_3)N(H)(CH_3)C_5H_5CH_3\text{-}\eta^4)Fe(CO)_3$ and $(OC)_3Cr(\eta^6\text{-}C_6H_5N(H)C_5H_6CH_3\text{-}\eta^4)Fe(CO)_3$ were determined by X-ray diffraction. © 1997 Elsevier Science S.A.

Keywords: Carbonyl chromium complexes; Carbonyl iron complexes; *N*-((*E*)-1-Methyl-2,4-pentadienyl)aniline; *N*-Methyl-*N*-((2*E*,4*E*)-1-methyl-2,4-hexadienyl)aniline

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1. Introduction

The nucleophilic addition to coordinated unsaturated hydrocarbons is one of the most important reactions in organometallic chemistry [2–8] and the use of amines as nucleophiles has been particularly well studied [8]. Of special interest is the addition of nucleophiles to coordinated open chain unsaturated hydrocarbons, e.g., in $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]^+$ or $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ for application in asymmetric synthesis [9]. The addition of amines to these cationic iron complexes has been studied by Maglio et al. [10] and Maglio and Palumbo [11]. Later, it was shown that addition to $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ strongly depends on the nature of the nucleophile. According to electron density calculations [12], sterically nondemanding nucleophiles, such as OH or primary amines, add to the substituted terminal C-5 of the dienyl ligand [12–14]. But nucleophiles with bulky groups, such as tertiary amines or triphenylphosphine [15,16], prefer an attack at the unsubstituted terminal carbon atom C-1 of the unsaturated hydrocarbon [14,17,18,15,16]. In the course of our studies on the directed synthesis of hydrocarbon bridged complexes, we recently reported the addition of various aniline tricarbonyl chromium complexes to cationic cyclohexadienyl iron and ruthenium complexes [1]. We now describe the reaction with the open chain dienyl complexes $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$.

2. Results and discussion

The compounds **1–8** are obtained by reaction of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ with at least two equivalents of the aniline tricarbonyl chromium complexes, using the second equivalent as a base for deprotonation. In the IR spectra, all complexes show the typical $\nu(CO)$ bands of a neutral diene tricarbonyl iron and a tricarbonyl chromium group [14–16,19]. Complexes **1–3** and **5, 6,**

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[1] For Part XLI, see Ref. [1].

[2] X-ray structural analyses.

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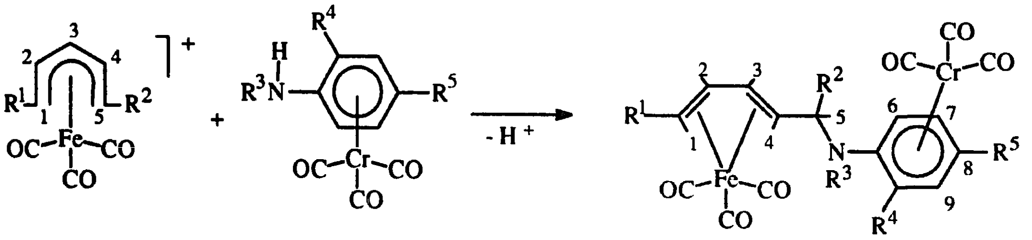
Table 1
Selected ^{1}H NMR shifts [ppm] of **1–8**

Compound	Olefinic H					H in α-position to NR^3	
1	5.58 (2-H)	5.29 (3-H)	1.42 (1-H)	1.10 (4-H)		3.21 (5-H)	
2	5.55 (2-H)	5.28 (3-H)	1.41–1.34 (1-H)	1.08 (4-H)		3.17 (5-H)	
3	5.67 (2-H)	5.28 (3-H)	1.29 (1-H)	1.29 (4-H)		3.35 (5-H)	
4	5.45 (2-H)	5.28 (3-H)	1.43–1.34 (1-H)	1.43–1.34 (4-H)			3.60 (5-H)
5	5.48 (2-H)	5.78 (3-H)	0.56 (1-H)	1.14 (4-H)	1.89 (1′-H)	3.29 (5-H)	
6	5.47 (2-H)	5.70 (3-H)	0.54 (1-H)	1.10 (4-H)	1.86 (1′-H)	3.23 (5-H)	
7	5.54 (4-H)	5.31 (3-H)	1.38 (5-H)	1.38 (2-H)		3.20 (1-H)	3.69 (1′-H)
8a	5.86–4.99 (2-H)	5.86–4.99 (3-H)	0.55–0.40 (1-H)	1.57–1.25 (4-H)	1.92–1.82 (1′-H)	3.55–3.22 (5-H)	
8b	5.86–4.99 (4-H)	5.86–4.99 (3-H)	1.57–1.25 (5-H)	1.57–1.25 (2-H)		3.55–3.22 (1-H)	3.55–3.22 (1′-H)

8 exhibit only one ν(NH) band in contrast to the starting aniline complexes. In complex **4** and **7** ν(NH) absorptions are absent as expected.

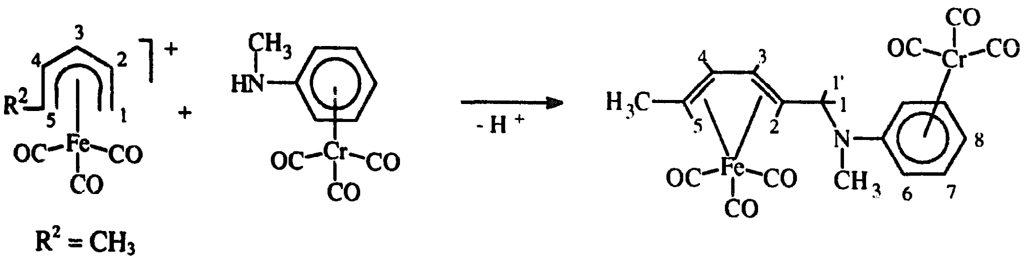
Due to the various chiral centres in **1–8** we would expect very complex NMR spectra, and we were astonished to find rather simple ones.



1-6

	R^1	R^2	R^3	R^4	R^5
1	CH_3	CH_3	H	H	H
2	CH_3	CH_3	H	H	CH_3
3	CH_3	CH_3	H	CH_3	H
4	CH_3	CH_3	CH_3	H	H
5	H	CH_3	H	H	H
6	H	CH_3	H	H	CH_3

Scheme 1.



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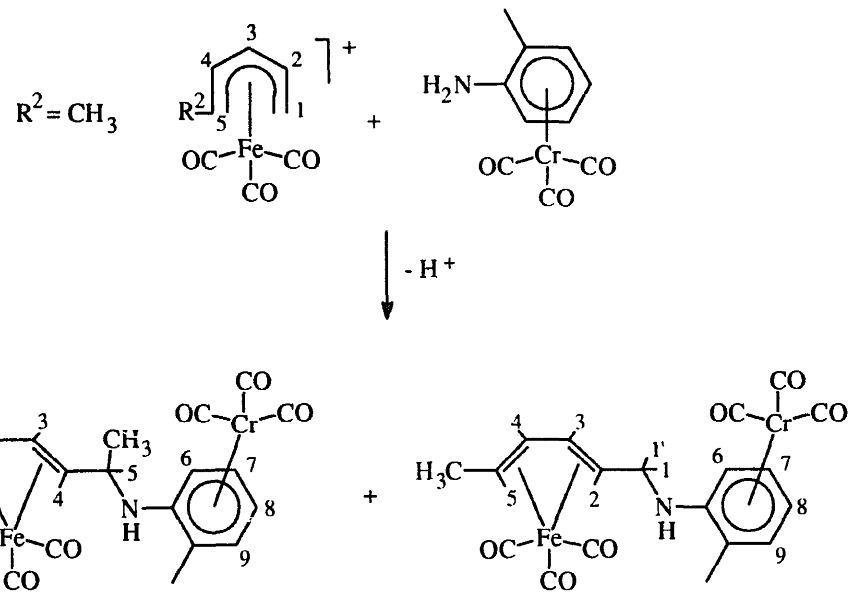
Scheme 2.



8a **8b**

Scheme 3.

The ${}^1H$ NMR spectra of **1–8** show the expected resonances for the aromatic system. The signals of the protons in α-position to the NR group exhibit a characteristic shift of 3.2–3.6 ppm (Table 1).

In the spectrum of **1** and **4**, the resolution is high enough to see the coupling between 5-H and 4-H, 5-CH_3 and the result is a doublet of quartets as expected. The olefinic protons 1-H and 4-H of **1–4** give resonances at about 1.4–1.1 ppm.

The reaction of the unsymmetrical $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ with the aniline tricarbonyl chromium complexes should depend on the different steric needs of the nucleophiles. The ${}^1H$ NMR spectra of **5** and **6** are very similar to those of **1** and **2**, but the signals for 1-H appear at higher field (Table 1). Additionally, the spectra of **5** and **6** exhibit a resonance of a second terminal olefinic proton (1′-H) at 1.89–1.86 ppm and also only one signal for the 5-H in α position of

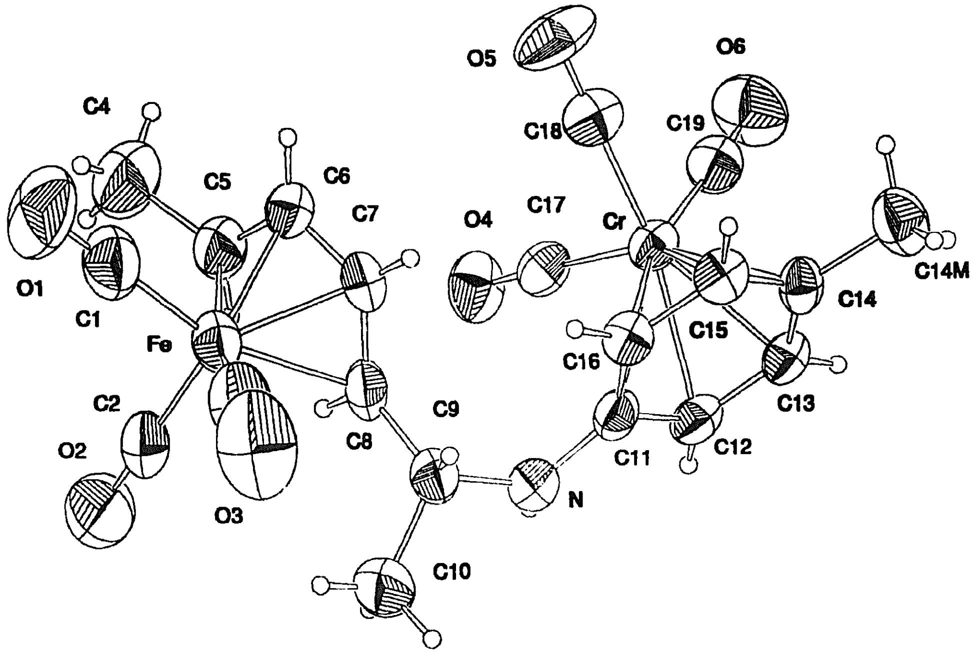


Fig. 1. Molecular structure of **2** in the crystal. Selected bond lengths [Å] and angles [°]: N–C9 1.452(7), N–C11 1.373(7); C9–N–C11 126.7(5).

the NH group. This indicates that the sterically nondemanding $(\eta^6\text{-}C_6H_5NH_2)Cr(CO)_3$ and $(\eta^6\text{-}p\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$ add at the methyl substituted terminal carbon of the dienyl ligand in $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ (Scheme 1).

The resonances for the olefinic H atoms in the ^1H NMR spectrum of **7** fit with those of **1–4**. In contrast to **5** and **6**, the signal for a second terminal olefinic proton is absent, but there are two resonances for H atoms in α-position to the NCH_3 group at 3.20 ppm (similar to **1–6**) and a new one at 3.69 ppm (Table 1). This can be explained by an attack of the bulky nucleophile $(\eta^6\text{-}C_6H_5N(H)CH_3)Cr(CO)_3$ at the unsubstituted end of the pentadienyl ligand (Scheme 2), to give a diastereotopic CH_2 group in 1-position with a ^2J coupling of about 15 Hz.

The addition of the planar chiral [20] $(\eta^6\text{-}o\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$ to $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]^+$ gives a mixture of products which could not be separated. A complete interpretation of the ^1H NMR spectrum is not possible. However, there is a resonance at 1.92–1.89 ppm with an intensity of two, indicating a second terminal olefinic proton and the signal for the 1-H is shifted upfield to 0.55–0.40 ppm (Table 1). This is very similar to the resonances of 1'-H and 1-H of **5** and **6**. But the ^1H NMR spectrum of **8** also exhibits a signal at 3.55–3.22 ppm with an intensity of four for the hydrogen in α-position of the NH group. This indicates that **8** is a mixture of **8a** and **8b** in a 2:1 ratio (Scheme 3).

Due to its very complex nature, **8a** is formed as a mixture of two diastereomers, to double the intensity of the resonance of 1'-H. It seems reasonable to assume that the sterical demand of the $o\text{-}CH_3$ group leads to partial attack at the less substituted terminus of the dienyl ligand, to give the minor regioisomer **8b**.

Fig. 1 shows the molecular structure of **2**.

According to Ref. [21], we would expect two different N–C bond lengths and a CNC angle between 109 and 120°, due to the electron withdrawing effect of the $Cr(CO)_3$ group [22]. In fact, the N–C-diene bond (1.452(7) Å) is longer than the N–C-arene bond (1.373(7) Å). The CNC angle is expanded to 126.7(5)°, presumably on steric reasons.

The molecular structure of **5** is shown in Fig. 2, proving that addition occurred at the substituted end of the dienyl ligand.

The bond features at the N atom seems to be very similar to **2**. The N–C-arene bond (1.359(5) Å) is shorter than the N–C-diene bond (1.469(5) Å) and the observed CNC angle is 124.9(4)°. Since these values are within the 4σ of the corresponding parameters of **2**, we consider that the steric and electronic effects in **2** and **5** are similar.

3. Experimental

$[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]BF_4$, $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]BF_4$ and the aniline tricarbonyl chromium complexes were prepared according to published procedures [19,23–25]. All operations were carried out under argon, using Schlenck-technique. Solvents were dried by distillation from sodium/benzophenone or $LiAlH_4$ solution. The ^1H NMR spectra were recorded on a Jeol GSX 270 (270.17 MHz) or a Jeol EX 400 (399.78 MHz). The observed coupling constants are

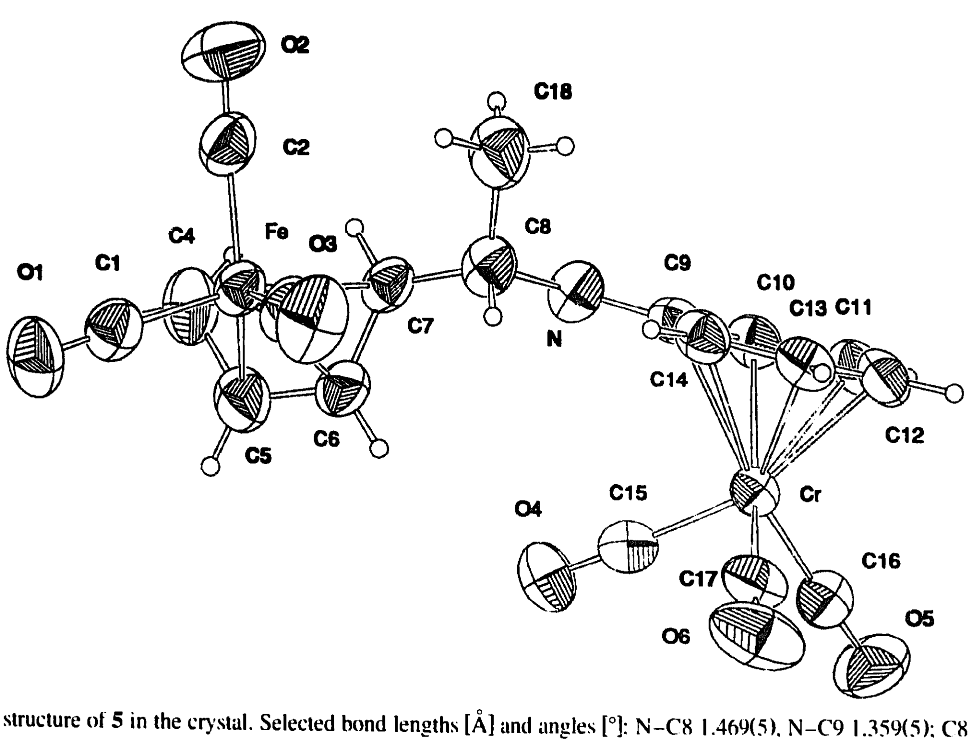


Fig. 2. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: N–C8 1.469(5), N–C9 1.359(5); C8–N–C9 124.9(4).

only absolute values. C, H, N analyses were performed on a Heraeus VT, IR spectra on a Perkin–Elmer 841. X-ray Structure Determinations: Siemens P4 diffractometer, MoK_α-radiations with graphite monochromator, ω-scan, $T = 293(2)$ K.

3.1. General procedure for the synthesis of **1–8**

The aniline tricarbonyl chromium complex was dissolved in 5 ml of THF and added to the dienyl tricarbonyl iron complex in 1.5 ml of THF at −78°C under rapid stirring. After 1 h the reaction mixture was warmed up to room temp and stirred for another 12 h. Then the solvent was removed in vacuo, to give a yellow oil. It was purified by column chromatography on SiO_2, using *n*-pentane/diethylether (3:2) as eluent. Evaporating the solvent under reduced pressure yielded a pale yellow powder which can be recrystallized from *n*-pentane for further purification. *p*-Methylaniline derivatives were only washed with pentane due to their poor solubility. Crystals for X-ray diffraction were grown from diethylether solution.

1: 33.9 mg (0.105 mmol) of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]BF_4$, 50.7 mg (0.221 mmol) of $(H_2NC_6H_5)Cr(CO)_3$, yield: 32.0 mg (66%). Anal. Found: C, 49.60; H, 5.94; N 3.36. $C_{19}H_{17}NO_6CrFe$ (463.2) Calcd.: C, 49.27; H, 3.70; N 3.02%. IR (cm^{-1}, nujol): 3397 m (NH), 2049 s (FeCO), 1989 s (FeCO), 1973 vs. (FeCO), 1951 vs. (CrCO), 1866 vs. (CrCO), 1548 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.77 (t, 2 H, 7-H, $^3J_{67} = {}^3J_{78} = 6.6$ Hz), 5.65 (m, 1 H, NH), 5.58 (dd, 1 H, 2-H, $^3J_{21} = 8.5$ Hz, $^3J_{23} = 4.7$ Hz), 5.29 (m, 1 H, 3-H), 5.10 (m, 2 H, 6-H), 4.96 (t, 1 H, 8-H, $^3J_{87} = 6.2$ Hz), 3.21 (dq, 1 H, 5-H, $^3J_{54} = 9.2$ Hz, $^3J_{5,5\text{-Me}} = 6.8$ Hz), 1.42 (s, 4 H, 1-CH_3, 1-H), 1.37 (d, 3 H, 5-CH_3, $^3J_{5,5\text{-Me}} = 6.2$ Hz), 1.10 (t, 1 H, 4-H, $^3J_{43} = {}^3J_{45} = 9.7$ Hz).

2: 34.3 mg (0.107 mmol) of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]BF_4$, 55.0 mg (0.226 mmol) of $(p\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$, yield: 28.2 mg (55%). Anal. Found: C, 49.02; H, 4.02; N, 3.03. $C_{20}H_{19}NO_6CrFe \cdot 0.7\ H_2O$ (489.8) Calcd.: C, 49.04; H, 4.20; N, 2.86%. IR (cm^{-1}, nujol): 3389 m (NH), 2053 s (FeCO), 1980 vs. (FeCO), 1959 vs. (FeCO), 1938 vs. (CrCO), 1862 vs. (CrCO), 1837 vs. (CrCO), 1560 m (NH or C=C), 1517 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.70 (m, 2 H, 7-H), 5.55 (dd, 1 H, 2-H, $^3J_{21} = 8.6$ Hz, $^3J_{23} = 4.9$ Hz), 5.28 (dd, 1 H, 3-H, $^3J_{32} = 4.9$ Hz, $^3J_{34} = 6.8$ Hz), 5.11 (m, 2 H, 6-H), 3.17 (m, 1 H, 5-H), 2.04 (s, 3 H, *p*-CH_3), 1.41-1.34 (m, 7 H, 1-CH_3, 1-H, 5-CH_3), 1.08 (m, 1 H, 4-H).

3: 33.2 mg (0.103 mmol) of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]BF_4$, 59.0 mg (0.243 mmol) of $(o\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$, yield: 14.9 mg (30%). Anal. Found: C, 48.20; H, 4.26; N 2.76. $C_{20}H_{19}NO_6CrFe \cdot 1.2\ H_2O$ (498.8) Calcd.: C, 48.16; H, 4.32; N, 2.81%. IR (cm^{-1}, nujol): 3412 m (NH), 2047 s (FeCO), 1979 s (FeCO), 1956 s (FeCO), 1934 s (CrCO), 1841 s (CrCO), 1549 m (NH or C=C), 1533 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.79 (m, 1 H, aromatic H), 5.67 (m, 2 H, 2-H, NH), 5.28 (m, 2 H, 3-H, aromatic H), 4.97 (m, 2 H, aromatic H), 3.35 (m, 1 H, 5-H), 2.11 (s, 3 H, *o*-CH_3), 1.42 (m, 6 H, 1-CH_3, 5-CH_3), 1.29 (m, 2 H, 1-H, 4-H).

4: 64.6 mg (0.201 mmol) of $[(\eta^5\text{-}H_3CC_5H_5CH_3)Fe(CO)_3]BF_4$, 113.6 mg (0.467 mmol) of $(H_3CNHC_6H_5)Cr(CO)_3$, yield: 62.9 mg (66%). Anal. Found: C, 48.65; H, 4.44; N, 2.51. $C_{20}H_{19}NO_6CrFe \cdot 1\ H_2O$ (495.2) Calcd.: C, 48.51; H, 4.27; N, 2.83%. IR (cm^{-1}. nujol): 2050 s (FeCO), 1983 vs. (FeCO), 1968 s (FeCO), 1933 vs. (CrCO), 1866 s (CrCO), 1855 s (CrCO), 1839 s (CrCO), 1548 m (C=C). ^1H NMR (δ, 400 MHz, acetone-d_6 = 2.04): 5.81 (t, 2 H, 7-H, $^3J_{76} = {}^3J_{78} = 6.6$ Hz), 5.45 (dd, 1 H, 2-H, $^3J_{21} = 8.0$ Hz, $^3J_{23} = 5.2$ Hz), 5.28 (dd, 1 H, 3-H, $^3J_{32} = 4.8$ Hz, $^3J_{34} = 8.4$ Hz), 5.21 (d, 1 H, 6-H, $^3J_{67} = 7.2$ Hz), 5.13 (d, 1 H, 6′-H, $^3J_{6'7} = 7.2$ Hz), 5.01 (t, 1 H, 8-H, $^3J_{87} = 6.4$ Hz), 3.60 (dq, 1 H, 5-H, $^3J_{54} = 8.6$ Hz, $^3J_{5,5\text{-Me}} = 6.8$ Hz), 2.80 (s, 3 H, NCH_3), 1.43–1.34 (m, 8 H, 1-CH_3, 1-H, 4-H, 5-CH_3).

5: 79.2 mg (0.257 mmol) of $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]BF_4$, 129.3 mg (0.564 mmol) of $(H_2NC_6H_5)Cr(CO)_3$, yield: 45.3 mg (39%). Anal. Found: C, 47.88; H, 2.99; N, 3.20. $C_{18}H_{15}NO_6CrFe$ (449.2) Calcd.: C, 48.13; H, 3.37; N, 3.12%. IR (cm^{-1}, nujol): 3396 w (NH), 2052 s (FeCO), 1976 s (FeCO), 1956 s (FeCO), 1937 s (CrCO), 1857 s (CrCO), 1545 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.78 (m, 3 H, 7-H, 3-H), 5.48 (dddd, 1 H, 2-H , $^3J_{21} = 7.0$ Hz, $^3J_{21'} = 9.5$ Hz, $^3J_{23} = 4.9$ Hz, $^4J_{24} = 1.1$ Hz), 5.12 (m, 2 H, 6-H), 4.97 (tt, 1 H, 8-H, $^3J_{87} = 6.2$ Hz, $^4J_{86} = 0.8$ Hz), 3.77 (s, 1 H, NH), 3.29 (ddq, 1 H, 5-H, $^3J_{54} = 9.0$ Hz, $^3J_{56} = 6.5$ Hz, $^4J_{53} = 2.4$ Hz), 1.89 (ddd, 1 H, 1′-H, $^3J_{1'2} = 7.0$ Hz, $^2J_{1'1} = 2.4$ Hz, $^4J_{1'3} = 1.1$ Hz), 1.40 (d, 3 H, 5-CH_3, $^3J_{5,5\text{-Me}} = 6.5$ Hz), 1.14 (ddd, 1 H, 4-H, $^3J_{43} = 17.8$ Hz, $^3J_{45} = 8.9$ Hz, $^4J_{42} = 1.1$ Hz), 0.56 (ddd, 1 H, 1-H, $^3J_{12} = 9.5$ Hz, $^2J_{11'} = 2.2$ Hz, $^4J_{13} = 1.1$ Hz).

6: 60.7 mg (0.198 mmol) of $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]BF_4$, 105.5 mg (0.434 mmol) of $(p\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$, yield: 52.9 mg (58%). Anal. Found: C, 48.30; H, 3.63; N, 2.92. $C_{19}H_{17}NO_6CrFe$ (463.2) Calcd.: C, 49.27; H, 3.70; N, 3.02%. IR (cm^{-1}, nujol): 3402 m (NH), 2053 s (FeCO), 1984 s (FeCO), 1965 s (FeCO), 1937 s (CrCO), 1862 s (CrCO), 1835 s (CrCO), 1568 m (NH or C=C), 1517 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.70 (m, 3 H, 7-H, 3-H), 5.47 (m, 1 H, 2-H), 5.11 (m, 2 H, 6-H), 3.76 (m, 1 H, NH), 3.23 (m, 1 H, 5-H), 2.02 (s, 3 H, *p*-CH_3), 1.86 (m, 1 H, 1′-H), 1.37 (m, 3 H, 5-CH_3), 1.10 (m, 1 H, 4-H), 0.54 (m, 1 H, 1-H).

7: 66.6 mg (0.216 mmol) of $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]BF_4$, 107.1 mg (0.440 mmol) of

$(H_3CNHC_6H_5)Cr(CO)_3$, yield: 35.3 mg (35%). Anal. Found: C, 49.66; H, 3.93; N, 3.09. $C_{19}H_{17}NO_6CrFe \cdot 1\ H_2O$ (463.2) Calcd.: C, 49.27; H, 3.70; N, 3.02%. IR (cm^{-1}, nujol): 2049 s (FeCO), 1975 s (FeCO), 1934 s (CrCO), 1842 s (CrCO), 1545 m (C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.82 (m, 2 H, 7-H), 5.54 (dd, 1 H, 4-H, $^3J_{43} = 8.1$ Hz, $^3J_{45} = 5.4$ Hz), 5.31 (dd, 1 H, 3-H, $^3J_{34} = 5.4$ Hz, $^3J_{32} = 8.1$ Hz), 5.18 (m, 2 H, 6-H), 5.01 (t, 1 H, 8-H, $^3J_{87} = 6.1$ Hz), 3.69 (dd, 1 H, 1′-H, $^3J_{1'2} = 3.2$ Hz, $^2J_{1'1} = 15.4$ Hz), 3.20 (dd, 1 H, 1-H, $^3J_{12} = 8.9$ Hz, $^2J_{11'} = 15.7$ Hz), 3.00 (s, 3 H, NCH_3), 1.42 (d, 3 H, 5-CH_3, $^3J_{5,5\text{-Me}} = 5.7$ Hz), 1.38 (m, 2-H, 5-H).

8: 76.9 mg (0.250 mmol) of $[(\eta^5\text{-}C_5H_6CH_3)Fe(CO)_3]BF_4$, 128.1 mg (0.527 mmol) of $(o\text{-}H_3CC_6H_4NH_2)Cr(CO)_3$, yield: 50.1 mg (43%). Anal. Found: C, 49.30; H, 3.60; N, 3.04. $C_{19}H_{17}NO_6CrFe$ (463.2) Calcd.: C, 49.27; H, 3.70; N. 3.02%. IR (cm^{-1}, nujol): 3424 s (NH), 2049 s (FeCO), 1980 s (FeCO), 1948 sh (CrCO), 1879 s (CrCO), 1545 m (NH or C=C). ^1H NMR (δ, 270 MHz, acetone-d_6 = 2.04): 5.86–4.99 (m, 18 H, **8a**: 2-H, 3-H, 6-H–9-H both diastereoisomers, **8b**: 3-H, 4-H, 6-H–9-H), 3.55–3.22 (m, 4 H, **8a**: 5-H both diastereoisomers, **8b**: 1-H, 1′-H), 2.17–2.10 (m, 9 H, **8a**: o-CH_3 both diastereoisomers, **8b**: o-CH_3), 1.92–1.82 (m, 2 H, **8a**: 1′-H both diastereoisomers), 1.57–1.25 (m, 13 H, **8a**: 4-H, 5-CH_3 both diastereoisomers, **8b**: 5-CH_3, 2-H, 5-H), 0.55–0.40 (m, 2 H, **8a**: 1-H both diastereoisomers).

3.2. X-ray structure determination of 2 [3]

$C_{20}H_{19}CrNO_6Fe$, $M = 477.21$, $T = 293(2)$ K, monoclinic, P2(1)/c, crystal size 0.38 × 0.27 × 0.05 mm, $a = 22.628(2)$, $b = 7.7610(10)$, $c = 11.9660(10)$ Å, $\alpha = 90$, $\beta = 90.080(10)$, $\gamma = 90°$, $V = 2101.4(4)$ Å^3, $Z = 4$, d(calcd.) = 1.508 g/cm^3, $\mu = 1.242$ mm^{-1}, $F(000) = 976$, Θ range 2.70–24.98°, index ranges $+h+k\pm l$, $-h-k\pm l$; 5594 collected reflections, 2663 independent reflections ($R_{int} = 0.0400$), data/restraints/parameters: 2662/0/265, GOF = 1.036, $R1 = 0.0468$, $wR2 = 0.0961$; largest diff. peak/hole = 0.315/−0.243 e Å^{-3}.

3.3. X-ray structure determination of 5 [3]

$C_{18}H_{15}CrNO_6Fe$, $M = 449.16$, $T = 293(2)$ K, triclinic, P1, crystal size 0.25 × 0.18 × 0.05 mm, $a = 6.8170(10)$, $b = 11.2390(2)$, $c = 12.6960(2)$ Å, $\alpha = 96.060(10)$, $\beta = 102.050(10)$, $\gamma = 100.380(10)°$, $V = 925.3(2)$ Å^3, $Z = 2$, d(calcd.) = 1.612 g/cm^3, $\mu = 1.405$ mm^{-1}, $F(000) = 456$, Θ range 2.30–25.00°, index ranges $-8 \le h \le 8$; $-13 \le k \le 13$; $-15 \le l \le 15$, 6515 collected reflections, 3258 independent reflections ($R_{int} = 0.0512$), data/restraints/parameters: 3258/0/263, GOF = 1.011, $R1 = 0.0428$, $wR2 = 0.0863$, largest diff. peak/hole = 0.329/−0.273 e Å^{-3}.

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[3] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. +44(0)1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk).