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Nucleophilic addition of chromium carbene anions to the coordinated olefin in $[Cp(CO)_2Fe(\eta^2\text{-olefin})]^+$ complexes and to the cyclohexadienyl ligand in $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$

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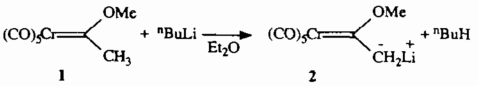
Abstract

The chromium carbene anion $[(CO)_5Cr{=}C(OMe)CH_2]^-$ (**2**) has been found to add to the coordinated olefin in the complexes $[(Cp(CO)_2Fe(\eta^2\text{-olefin})]^+$ (olefin = *cis*-2-butene, *trans*-2-butene, styrene) to form bimetallic chromium–iron complexes of the form $(CO)_5Cr{=}C(OMe)CH_2{-}CHR{-}CHR'{-}Fe(CO)_2Cp$. Complex **2** also adds to the cyclohexadienyl ligand in $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ to form a crystallographically characterized bimetallic complex which has a $Fe(CO)_3$ unit coordinated to a $[(CO)_5Cr{=}C(OMe)CH_2]^-$ substituted cyclohexadiene ligand. A trimetallic Fe_2Cr complex with two $(\eta^4\text{-cyclohexadiene})Fe(CO)_3$ groups attached to the β-carbon of the carbene ligand of the $(CO)_5Cr{=}C(OMe)CH$ moiety has also been prepared, and two of the three possible stereoisomers of this complex have been crystallographically characterized.

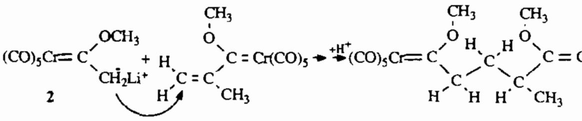
Introduction

It is now well recognized that hydrogen atoms alpha to the carbene carbon in many carbene complexes are acidic and can be removed by treatment with base. For example, Casey and co-workers originally reported that deprotonation of $(CO)_5Cr{=}C(OMe)CH_3$ (**1**) with ^nBuLi afforded the chromium carbene anion $Li[(CO)_5Cr{=}C(OMe)CH_2]$ (**2**), eqn. (1) [1]. Similar deprotonation reactions have since been observed for $(CO)_5W{=}C(OR)CH_2R$ [2] and $Cp(CO)_2Mn{=}C(OR)CH_2R$ [3], and the resultant carbene anions have been shown to react with a number of organic reagents [1]. Macomber and co-workers have recently extended these reactions to organometallic substrates and has demonstrated the preparation of a series of bimetallic complexes of chromium and tungsten having bridging bis(carbene) ligands using reactions like that illustrated in eqn. (2) [4].



$$(CO)_5Cr{=}C(OMe)CH_3 + {}^nBuLi \xrightarrow[Et_2O]{} (CO)_5Cr{=}C(OMe)CH_2^-Li^+ + {}^nBuH \qquad (1)$$

1 **2**



(2)

In the course of our studies aimed at the preparation of bimetallic complexes bridged by complex organic ligands, we considered the possibility of adding carbene anions to coordinated organic ligands on electrophilic metal complexes. Herein are described the synthesis and characterization of a series of bimetallic chromium–iron complexes formed by addition of the chromium carbene anion **2** to the coordinated olefin in a series of $[Cp(CO)_2Fe(\eta^2\text{-olefin})]^+$ complexes and to the cyclohexadienyl ligand in $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$. Also described is the synthesis of a trimetallic $CrFe_2$ complex with two $(\eta^4\text{-cyclohexadiene})Fe(CO)_3$ groups attached to the β-carbon of the carbene ligand of the $(CO)_5Cr{=}C(OMe)CH$ moiety. Two of the three possible stereoisomers of this latter complex have been crystallographically characterized. While the writing of this manuscript was in progress,

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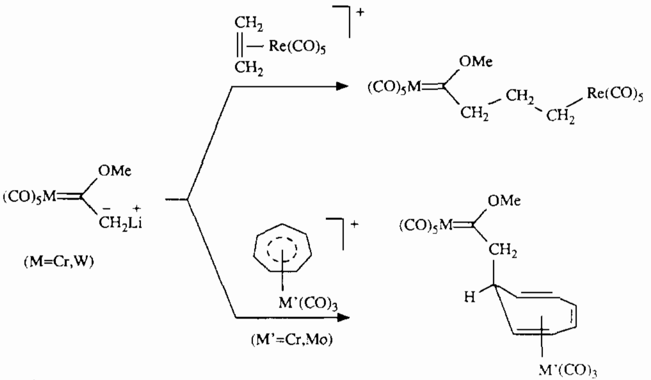
Beck and co-workers reported the closely related transformations shown in Scheme 1 [5].

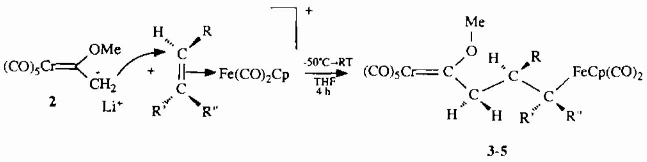


Scheme 1.

Results and discussion

Preparation of bimetallic chromium–iron carbene alkyl complexes

Complex **2** has been found to be sufficiently nucleophilic to add to the coordinated olefin in $[Cp(CO)_2Fe(olefin)]^+$ complexes to give the bimetallic complexes **3**–**5** shown in Scheme 2. These compounds were isolated as yellow solids and have been spectroscopically characterized. Each complex showed IR ν(CO) bands indicating the presence of $Cr(CO)_5$ and $CpFe(CO)_2$ units (see 'Experimental'), and complexes **3** and **4** showed $M^+ - CO$ ions in their electron impact mass spectra. For **5**, the highest mass ion observed was $M^+ - 6CO$, apparently because of the decreased volatility of this complex and the high probe temperature needed to induce its vaporization. ^1H and ^{13}C NMR spectral data for **3**–**5** are given in 'Experimental'. Each compound showed characteristic methoxy and Cp resonances along with resonances due to the protons of the bridging ligand. For example, compound **3** showed an ABX pattern for the CH_2 protons centered at δ 3.42, a multiplet at δ 2.42 for the proton on the carbon β to the iron atom, a doublet of quartets at δ 2.91 for proton in the R′ position, and doublets at δ 0.92 and 1.23 for the R and R″ methyl groups, respectively.



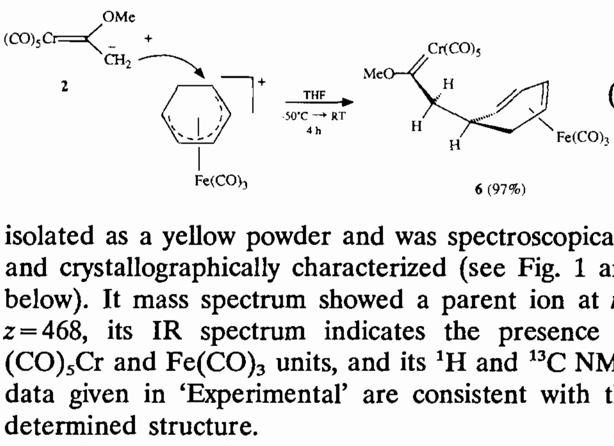
Compound	R	R′	R″	Yield (%)
3	CH_3	H	CH_3	45
4	CH_3	CH_3	H	37
5	Ph	H	H	49

Scheme 2.

The ^1H NMR data also indicated the absence of isomerization of the olefin during the addition reactions of Scheme 2. Thus, complex **3** was produced as a single diastereomer when the reaction was conducted with the *cis*-2-butene complex, and similarly **4** formed as a single diastereomer when the reaction was conducted with the *trans*-2-butene complex. The absence of crossover to give a mixture of these two compounds in the separate reactions indicates the absence of rotation about the C–C bond of the olefin during the addition reaction. We presume that the reaction occurs by *trans* attack of the chromium carbene anion on the coordinated olefin, since Rosenblum and co-workers have shown that the olefin ligand in a series of $[Cp(CO)_2Fe(\eta^2\text{-olefin})]^+$ complexes undergoes clean *trans* attack by a variety of organic nucleophiles [6].

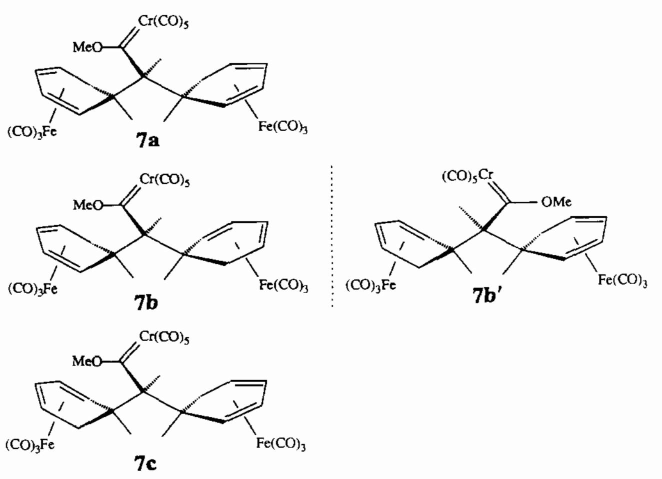
Addition of $[(CO)_5Cr{=}C(OMe)CH_2]^-$ to the cyclohexadienyl ligand of $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$

Like typical organic nucleophiles [7], complex **2** was found to add to the cyclohexadienyl ligand of $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$ to give the bimetallic complex **6** shown in eqn. (3) which possesses a $(CO)_5Cr{=}C(OMe)CH_2$-substituted cyclohexadiene ligand coordinated to an $Fe(CO)_3$ unit. Complex **6** was isolated as a yellow powder and was spectroscopically and crystallographically characterized (see Fig. 1 and below). It mass spectrum showed a parent ion at $m/z = 468$, its IR spectrum indicates the presence of $(CO)_5Cr$ and $Fe(CO)_3$ units, and its ^1H and ^{13}C NMR data given in 'Experimental' are consistent with the determined structure.



(3)

In the course of repeating the preparation of **6**, a trimetallic Fe_2Cr complex was serendipitously discovered. A rational synthesis of this compound **7** was then developed by successively treating **6** with ^nBuLi and $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$, eqn. (4). The ^nBuLi deprotonates the methylene carbon that links the carbene carbon and the cyclohexadiene ligand of **6** to generate the carbene anion **8** which in turn adds to a ring carbon of $[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$ when treated with this reagent. Complex **7** has three chiral centers and as a result can exist as a pair of enantiomers (**7b**, **7b′**) or in the two *meso* forms **7a** and **7c** drawn in Scheme 3. Two of these, **7a** and **7b**/**7b′**, were isolated



Scheme 3.

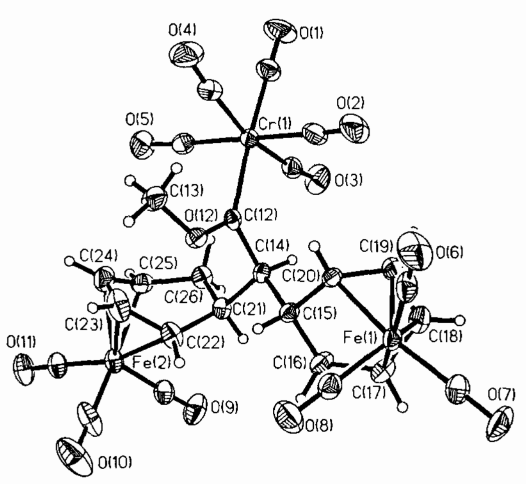


Fig. 2. An ORTEP drawing for **7a**.

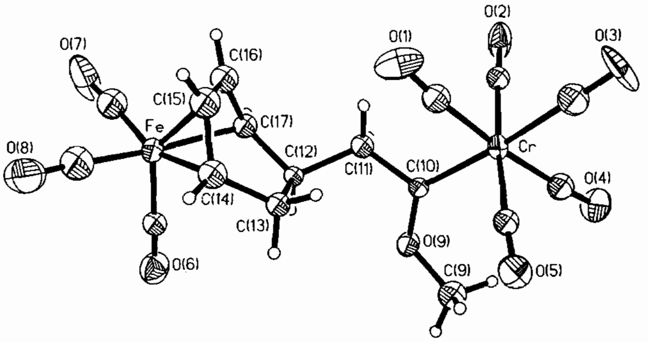


Fig. 1. An ORTEP drawing for **6**.

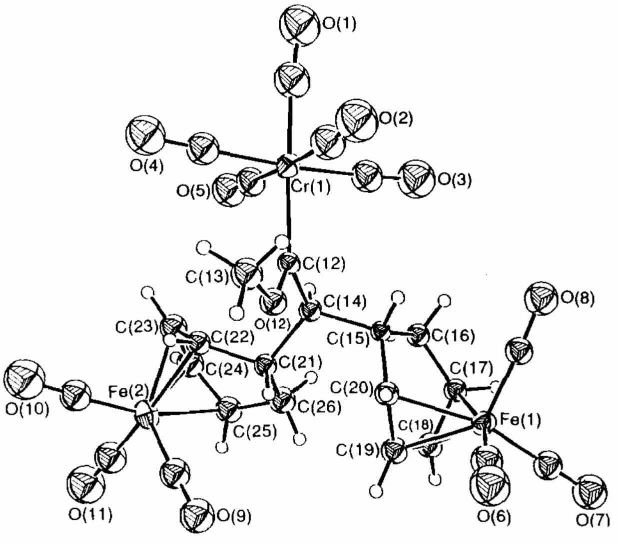
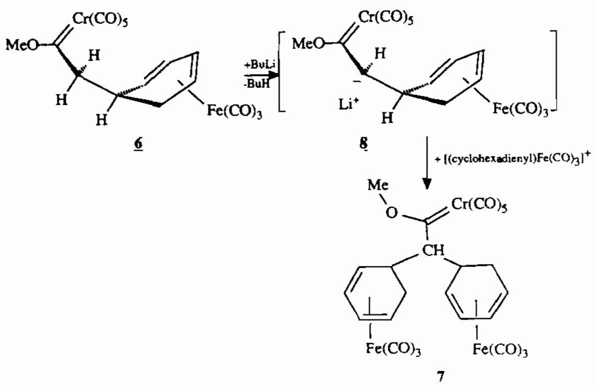


Fig. 3. An ORTEP drawing for **7b**.



(4)

and separately characterized by X-ray crystallography (see Figs. 2 and 3), and their spectroscopic data given in 'Experimental' are consistent with the determined structures. Although **7c** could possibly form in this reaction, we were unable to obtain any NMR evidence for its presence.

Crystallographic characterization of complexes 6, 7a and 7b·CH_2Cl_2

ORTEP drawings of these three molecules are given in Figs. 1–3, respectively, and the pertinent crystallographic data are set out in Tables 1–7. Compound **6** can be described as having a $(CO)_5Cr{=}C(OMe)CH_2$-substituted cyclohexadiene ligand coordinated to a $Fe(CO)_3$ unit. As expected for the method of synthesis used, the structure shows the chromium carbene moiety to be located on the *exo* face of the coordinated cyclohexadiene ring [7]. The molecule is chiral at the C(12) carbon atom and both enantiomers are present in the unit cell of the centrosymmetric space group. All metric parameters within the chromium carbene moiety and within the iron cyclohexadiene moiety are normal [8, 9].

Compound **7a** derives from **6** by substitution of one hydrogen atom on the α-carbon atom of the carbene moiety by a second cyclohexadienyl tricarbonyl iron unit. As for **6**, the chromium carbene moiety is located

TABLE 1. Crystal, data collection and refinement parameters for **6a**, **7a** and **7b**·CH_2Cl_2[a]

	6	**7a**	**7b**·CH_2Cl_2
Crystal parameters			
Formula	$C_{17}H_{12}O_9CrFe$	$C_{26}H_{18}CrFe_2O_{12}$	$C_{27}H_{20}Cl_2CrFe_2O_{12}$
Formula weight	468.12	686.10	771.05
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	21.699(8)	9.085(3)	12.240(2)
b (Å)	7.054(3)	9.122(2)	10.526(1)
c (Å)	12.740(4)	17.410(6)	24.779(3)
α (°)		89.57(2)	
β (°)	95.83(3)	75.48(2)	94.54(1)
γ (°)		85.04(2)	
V (Å^3)	1940.0(13)	1385.2(8)	3182.5(8)
Z	4	2	4
μ(Mo Kα) (cm^{-1})	13.54	14.75	14.82
D_{calc} (g cm^{-3})	1.603	1.645	1.609
Color	yellow	yellow	yellow
Size (mm)	0.26×0.24×0.40	0.26×0.30×0.52	not measured
Temperature (K)	296	296	298
Data collection			
Diffractometer	Siemens P4	Siemens P4	Enraf Nonius CAD4
Monochromator	graphite	graphite	graphite
Scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Wavelength, λ (Å)	0.71073	0.71073	0.71073
Radiation	Mo Kα	Mo Kα	Mo Kα
Data collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
2θ Scan limits (°)	4–45	4–52	2–40
Scan speed (° min^{-1})	var. 4–20	var. 6–20	var. 2–10
Reflections collected	2918	5511	3136
Unique reflections	2519	5326	3072
Unique ($n\sigma(F_o)$)	1259 ($n=4$)	3518 ($n=4$)	1541 ($n=2$)
T_{max}/T_{min}	N.A.	N.A.	1/0.78
R_{int} (%)	2.57	2.11	1.70
Standard reflections	3/197	3/197	3/2 h
Decay (%)	~35	~1	31
Refinement			
$R(F)$ (%)	9.0	5.2	6.5
$R(wF)$ (%)	9.5	5.0	6.9
$\Delta(\rho)_{max}$ (e Å^{-3})	0.70	0.64	0.6
Δ/σ_{max}	0.12	0.08	0.14
GOF	1.830	1.240	4.2
N_o/N_v	7.50	9.20	7.62

[a] $R(F)=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R(wF)=\Sigma(w^{1/2}(|F_o|-|F_c|))/(w^{1/2}|F_o|)$; $GOF=[\Sigma w||F_o|-|F_c||/N_o-N_v]^{1/2}$.

on the *exo* faces of both coordinated cyclohexadiene rings. Owing to the fact that C(15) and C(21) bear the same substituents and show opposite configurations, *R*(*S*) and *S*(*R*), respectively, the molecule is one of the two possible *meso* forms (see Scheme 3) and is not chiral. Compound **7b** has basically the same structure as **7a** but differs from **7a** by an inversion of configuration of the C(15) carbon atom. As a consequence, the overall molecule is now chiral. However, since **7b** crystallizes in a centrosymmetric space group, both enantiomers are present in the crystal cell. As for **6**, all metric parameters with **7a** and **7b** are normal and in the range expected for such complexes.

Experimental

General

The complexes $(CO)_5Cr{=}C(OMe)Me$ [10], $[Cp(CO)_2Fe(\eta^2\text{-olefin})][BF_4]$ [11] and $[Fe(CO)_3(C_6H_7)][BF_4]$ [12] were prepared by the literature procedures. The reagent ^{n}BuLi (1.6 M solution in hexanes) was purchased from Aldrich Chemical Co. and used as received. Solvents were dried by refluxing over Na/benzophenone ketyl (tetrahydrofuran (THF), Et_2O), CaH_2 (CH_2Cl_2, pentane and hexane), or K_2CO_3 (acetone) and were freshly distilled prior to use. All manipulations were performed using standard Schlenk

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **6**

	x	y	z	U_{eq}[a]
Cr	6385(1)	1581(4)	7398(2)	36(1)
Fe	8973(1)	−2088(5)	5196(2)	59(1)
O(1)	7552(7)	3657(20)	6998(12)	86(7)
O(2)	6947(6)	441(21)	9587(11)	76(6)
O(3)	5989(8)	5263(22)	8366(11)	104(8)
O(4)	5241(6)	−330(24)	8105(11)	88(7)
O(5)	5679(6)	2767(19)	5325(10)	64(6)
O(6)	8347(6)	−5261(22)	4174(12)	76(6)
O(7)	10065(8)	−4042(35)	6207(11)	162(12)
O(8)	9630(9)	−860(39)	3418(13)	186(13)
O(9)	6479(5)	−2172(16)	6193(9)	43(4)
C(1)	7109(9)	2855(29)	7107(14)	51(5)
C(2)	6751(8)	873(26)	8759(15)	40(5)
C(3)	6131(9)	3903(33)	7994(17)	63(6)
C(4)	5657(9)	411(28)	7783(15)	51(5)
C(5)	5960(8)	2283(27)	6104(14)	41(5)
C(6)	8579(8)	−4018(29)	4574(15)	43(6)
C(7)	9629(10)	−3222(32)	5833(16)	70(6)
C(8)	9386(10)	−1404(34)	4155(18)	77(7)
C(9)	5849(8)	−2181(28)	5820(14)	59(6)
C(10)	6733(7)	−813(26)	6775(12)	30(4)
C(11)	7406(7)	−1350(25)	7056(13)	41(5)
C(12)	7770(6)	−2003(23)	6101(11)	29(4)
C(13)	7692(7)	−626(25)	5142(13)	40(5)
C(14)	8317(8)	25(26)	4829(15)	55(6)
C(15)	8761(9)	608(31)	5640(16)	62(6)
C(16)	8827(8)	−599(29)	6534(15)	56(6)
C(17)	8450(7)	−2214(26)	6484(13)	42(5)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond lengths (Å) and angles (°) for **6**

Bond distances (Å)			
Cr–C(1)	1.878(20)	Cr–C(2)	1.899(18)
Cr–C(3)	1.911(23)	Cr–C(4)	1.892(20)
Cr–C(5)	1.872(18)	Cr–C(10)	2.043(18)
Fe–C(6)	1.753(20)	Fe–C(7)	1.759(22)
Fe–C(8)	1.742(24)	Fe–C(14)	2.081(18)
Fe–C(15)	2.050(22)	Fe–C(16)	2.054(20)
Fe–C(17)	2.090(17)	C(10)–O(9)	1.300(20)
O(9)–C(9)	1.402(2)	C(10)–C(11)	1.515(21)
C(11)–C(12)	1.586(22)	C(12)–C(13)	1.556(22)
C(13)–C(14)	1.525(25)	C(14)–C(15)	1.400(26)
C(15)–C(16)	1.417(28)	C(16)–C(17)	1.401(26)
C(17)–C(12)	1.512(20)		
Bond angles (°)			
C(1)–Cr–C(2)	91.5(8)	C(7)–Fe–C(16)	92.0(9)
C(1)–Cr–C(3)	87.1(9)	C(8)–Fe–C(16)	128.6(10)
C(2)–Cr–C(3)	88.5(8)	C(14)–Fe–C(16)	70.2(8)
C(1)–Cr–C(4)	175.7(8)	C(15)–Fe–C(16)	40.4(8)
C(2)–Cr–C(4)	86.0(8)	C(6)–Fe–C(17)	92.4(8)
C(3)–Cr–C(4)	89.3(9)	C(7)–Fe–C(17)	95.6(9)
C(1)–Cr–C(5)	92.7(8)	C(8)–Fe–C(17)	166.3(10)
C(2)–Cr–C(5)	175.1(8)	C(14)–Fe–C(17)	78.1(7)
C(3)–Cr–C(5)	89.2(9)	C(15)–Fe–C(17)	70.6(8)
C(4)–Cr–C(5)	89.6(8)	C(16)–Fe–C(17)	39.5(7)
C(1)–Cr–C(10)	88.3(8)	C(9)–O(9)–C(10)	122.6(13)
C(2)–Cr–C(10)	90.0(7)	Cr–C(10)–O(9)	132.8(11)
C(3)–Cr–C(10)	175.1(8)	Cr–C(10)–C(11)	120.0(11)
C(4)–Cr–C(10)	95.2(8)	O(9)–C(10)–C(11)	107.0(14)
C(5)–Cr–C(10)	92.6(7)	C(10)–C(11)–C(12)	115.8(12)
C(6)–Fe–C(7)	101.0(10)	C(11)–C(12)–C(13)	113.4(13)
C(6)–Fe–C(8)	97.9(10)	C(11)–C(12)–C(17)	109.1(12)
C(7)–Fe–C(8)	1.2(10)	C(13)–C(12)–C(17)	109.9(13)
C(6)–Fe–C(14)	99.4(8)	C(12)–C(13)–C(14)	111.3(13)
C(7)–Fe–C(14)	158.9(9)	Fe–C(14)–C(13)	109.4(12)
C(8)–Fe–C(14)	91.4(9)	Fe–C(14)–C(15)	69.0(11)
C(6)–Fe–C(15)	137.0(8)	C(13)–C(14)–C(15)	117.3(17)
C(7)–Fe–C(15)	119.3(9)	Fe–C(15)–C(14)	71.4(12)
C(8)–Fe–C(15)	95.8(10)	Fe–C(15)–C(16)	70.0(12)
C(14)–Fe–C(15)	39.6(7)	C(14)–C(15)–C(16)	115.1(18)
C(6)–Fe–C(16)	131.5(9)	Fe–C(16)–C(15)	69.6(12)
Fe–C(16)–C(17)	71.7(11)		
C(15)–C(16)–C(17)	116.1(16)		
Fe–C(17)–C(12)	109.4(10)		
Fe–C(17)–C(16)	68.8(11)		
C(12)–C(17)–C(16)	118.8(16)		

techniques under an N_2 atmosphere. IR spectra were recorded on IBM FTIR-32 and Perkin-Elmer 225 spectrophotometers operated in the absorbance mode. NMR spectra were obtained on a Bruker AM 300 FT NMR spectrometer, and mass spectra were recorded on AEI-MS9 (EI) and AFAB-MS9 (FAB) mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY and from the 'Service de Microanalyse du Laboratoire de Chimie de Coordination', Toulouse, France.

Addition of 2 to [Cp(CO)$_2$Fe(η^2-cis-2-butene)]BF$_4$ to form complex 3

The anionic carbene complex **2** was generated in THF (10 ml) at −50 °C from **1** (0.20 g, 0.8 mmol) and n-BuLi (0.55 ml of a 1.6 M solution in hexanes, 0.88 mmol). To this solution was added [Cp(CO)$_2$Fe(η^2-*cis*-2-butene)]BF$_4$ (0.33 g, 1.04 mmol) at −50 °C to induce a color change from yellow to a deep red after stirring for 3 h while slowly warming to room temperature. The THF was removed under vacuum to leave an orange oil which was chromatographed on neutral alumina with 1:4 CH_2Cl_2/pentane as eluent to yield a yellow band of **3**. Solvent evaporation from this fraction left a yellow oil which solidified to a yellow solid when permitted to stand under pentane for several hours, and this gave **3** in 45% yield (0.174 g, 0.36 mmol). A second red band of $[CpFe(CO)_2]_2$ was also eluted from the column with the same solvent mixture.

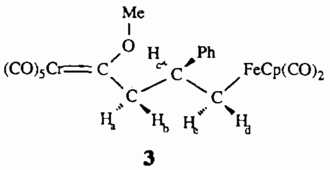


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TABLE 4. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for **7a**

	x	*y*	*z*	U_{eq}[a]
Cr(1)	8299(1)	−1493(1)	1926(1)	38(1)
Fe(1)	8131(1)	2960(1)	4752(1)	40(1)
Fe(2)	3604(1)	3916(1)	1399(1)	47(1)
O(1)	8902(7)	−4784(5)	1678(3)	92(3)
O(2)	10034(6)	−1547(6)	3211(3)	89(2)
O(3)	5435(6)	−2531(6)	3033(3)	77(2)
O(4)	11404(6)	−1515(6)	766(3)	95(2)
O(5)	6983(6)	−1140(6)	486(3)	81(2)
O(6)	11431(6)	2236(7)	4472(3)	93(3)
O(7)	7711(6)	4098(6)	6372(3)	87(2)
O(8)	8039(6)	5723(6)	3913(3)	83(2)
O(9)	968(6)	3532(7)	2731(3)	87(2)
O(10)	3998(6)	7034(7)	1511(4)	124(4)
O(11)	2025(6)	4392(6)	127(3)	75(2)
O(12)	8250(4)	1860(4)	1861(2)	40(1)
C(1)	8707(8)	−3548(7)	1765(4)	58(3)
C(2)	9341(8)	−1525(7)	2750(4)	57(3)
C(3)	6459(7)	−2052(6)	2629(3)	48(2)
C(4)	10230(8)	−1405(7)	1209(4)	57(3)
C(5)	7423(8)	−1287(6)	1047(4)	53(2)
C(6)	10142(8)	2525(7)	4595(3)	56(3)
C(7)	7899(7)	3638(7)	5743(4)	57(3)
C(8)	8108(7)	4661(7)	4246(3)	50(2)
C(9)	1996(8)	3718(7)	2213(4)	54(2)
C(10)	3832(9)	5832(9)	1459(5)	76(3)
C(11)	2656(7)	4198(7)	612(4)	53(2)
C(12)	7630(6)	691(6)	2192(3)	33(2)
C(13)	9535(7)	1788(7)	1171(3)	57(2)
C(14)	6256(6)	1295(6)	2852(3)	34(2)
C(15)	6707(6)	2411(6)	3421(3)	37(2)
C(16)	5351(6)	2897(7)	4120(3)	51(2)
C(17)	5774(7)	2775(7)	4904(3)	50(2)
C(18)	6561(7)	1445(7)	5073(3)	55(2)
C(19)	7751(7)	870(6)	4442(3)	47(2)
C(20)	8020(6)	1744(6)	3742(3)	36(2)
C(21)	4890(6)	2018(6)	2525(3)	37(2)
C(22)	5267(7)	3385(7)	2041(4)	51(2)
C(23)	5902(7)	3283(9)	1204(4)	69(3)
C(24)	5218(8)	2344(8)	798(4)	63(3)
C(25)	4041(7)	1599(7)	1270(3)	50(2)
C(26)	4215(7)	950(7)	2046(3)	48(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

3: *Anal.* Calc. for $C_{19}H_{18}CrFeO_8$: C, 47.33; H, 3.76. Found: C, 47.31; H, 3.78%. IR (CH_2Cl_2): ν(CO) = 2055(w), 1995(m), 1935(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.80 (s, 3H, OC*H*$_3$), 4.76 (s, 5H, Cp), 3.42 (ABX pattern, 2H, H_aH_b, *J*(HaHb) = 13.6 Hz, *J*(HaHc) = 5.4 Hz, *J*(HbHc) = 8.4 Hz), 2.91 (dq, 1H, H_d, *J*(HdHc) = 3.7 Hz, *J*(HdH(Me)) = 7.2 Hz), 2.42 (m, 1H, H_c), 1.23 (d, 3H, C*H*$_3$, *J*(HdH(Me)) = 7.2 Hz), 0.92 (d, 3H, C*H*$_3$, *J*(HcH(Me)) = 6.8 Hz). ^{13}C NMR (CD_2Cl_2): δ 365,2 (Cr=*C*), 224.0 (*trans*-Cr–*C*O), 218.8, 218.7 (Fe–*C*O), 217.1 (*cis*-Cr–*C*O), 86.7 (*C*$_5$H$_5$), 72.0 (Cr=C(OMe)*C*H$_2$), 68.2 (O*C*H$_3$), 44.2 (–CH$_2$*C*H(Me)), 25.1 (CH$_2$CH(Me)*C*H(Me)), 25.1 (CH$_2$CH(*C*H$_3$)), 17.1

TABLE 5. Selected bond lengths (Å) and angles (°) for **7a**

Bond distances (Å)			
Cr–C(1)	1.888(6)	Cr–C(2)	1.907(8)
Cr–C(3)	1.914(6)	Cr–C(4)	1.888(6)
Cr–C(5)	1.895(7)	Cr–C(12)	2.053(5)
Fe(1)–C(6)	1.787(7)	Fe(1)–C(7)	1.793(7)
Fe(1)–C(8)	1.780(7)	Fe(1)–C(17)	2.113(6)
Fe(1)–C(18)	2.047(7)	Fe(1)–C(19)	2.066(6)
Fe(1)–C(20)	2.113(5)	Fe(2)–C(9)	1.783(6)
Fe(2)–C(10)	1.784(8)	Fe(2)–C(11)	1.798(7)
Fe(2)–C(22)	2.116(7)	Fe(2)–C(23)	2.060(6)
Fe(2)–C(24)	2.047(6)	Fe(2)–C(25)	2.120(6)
C(12)–O(12)	1.311(6)	O(12)–C(13)	1.446(6)
C(12)–C(14)	1.534(6)	C(14)–C(15)	1.574(8)
C(14)–C(21)	1.583(8)	C(15)–C(16)	1.535(7)
C(16)–C(17)	1.509(9)	C(17)–C(18)	1.422(9)
C(18)–C(19)	1.402(7)	C(19)–C(20)	1.432(7)
C(20)–C(15)	1.520(8)	C(21)–C(22)	1.515(8)
C(22)–C(23)	1.427(9)	C(23)–C(24)	1.393(11)
C(24)–C(25)	1.399(9)	C(25)–C(26)	1.510(9)
C(21)–C(26)	1.546(9)		
Bond angles (°)			
C(1)–Cr(1)–C(2)	91.6(3)	C(2)–Cr(1)–C(4)	86.7(3)
C(1)–Cr(1)–C(3)	82.6(3)	C(3)–Cr(1)–C(4)	167.0(3)
C(2)–Cr(1)–C(3)	92.6(3)	C(1)–Cr(1)–C(5)	92.4(3)
C(1)–Cr(1)–C(4)	84.4(3)	C(2)–Cr(1)–C(5)	173.0(3)
C(3)–Cr(1)–C(5)	93.6(3)	C(19)–Fe(1)–C(20)	40.1(2)
C(4)–Cr(1)–C(5)	88.0(3)	C(9)–Fe(2)–C(10)	101.6(3)
C(1)–Cr(1)–C(12)	173.4(2)	C(9)–Fe(2)–C(11)	99.8(3)
C(2)–Cr(1)–C(12)	88.4(2)	C(10)–Fe(2)–C(11)	91.9(4)
C(3)–Cr(1)–C(12)	90.8(2)	C(9)–Fe(2)–C(22)	95.7(3)
C(4)–Cr(1)–C(12)	102.1(2)	C(10)–Fe(2)–C(22)	91.3(3)
C(5)–Cr(1)–C(12)	88.3(2)	C(11)–Fe(2)–C(22)	163.1(2)
C(6)–Fe(1)–C(7)	93.5(3)	C(9)–Fe(2)–C(23)	133.4(3)
C(6)–Fe(1)–C(8)	100.3(3)	C(10)–Fe(2)–C(23)	94.3(3)
C(7)–Fe(1)–C(8)	99.6(3)	C(11)–Fe(2)–C(23)	123.2(3)
C(6)–Fe(1)–C(17)	162.6(3)	C(22)–Fe(2)–C(23)	39.9(3)
C(7)–Fe(1)–C(17)	93.7(3)	C(9)–Fe(2)–C(24)	129.4(3)
C(8)–Fe(1)–C(17)	94.0(3)	C(10)–Fe(2)–C(24)	126.0(3)
C(6)–Fe(1)–C(18)	123.6(3)	C(11)–Fe(2)–C(24)	95.1(3)
C(7)–Fe(1)–C(18)	94.7(3)	C(22)–Fe(2)–C(24)	69.8(3)
C(8)–Fe(1)–C(18)	132.7(3)	C(23)–Fe(2)–C(24)	39.6(3)
C(17)–Fe(1)–C(18)	39.9(2)	C(9)–Fe(2)–C(25)	90.8(3)
C(6)–Fe(1)–C(19)	93.6(3)	C(10)–Fe(2)–C(25)	163.1(3)
C(7)–Fe(1)–C(19)	125.8(3)	C(11)–Fe(2)–C(25)	97.2(3)
C(8)–Fe(1)–C(19)	131.5(3)	C(22)–Fe(2)–C(25)	75.9(2)
C(17)–Fe(1)–C(19)	69.3(2)	C(23)–Fe(2)–C(25)	68.8(3)
C(18)–Fe(1)–C(19)	39.9(2)	C(24)–Fe(2)–C(25)	39.2(2)
C(6)–Fe(1)–C(20)	93.4(3)	C(12)–O(12)–C(13)	123.1(4)
C(7)–Fe(1)–C(20)	164.7(3)	Cr(1)–C(12)–O(12)	129.2(3)
C(8)–Fe(1)–C(20)	92.5(3)	Cr(1)–C(12)–C(14)	125.9(3)
C(17)–Fe(1)–C(20)	76.0(2)	O(12)–C(12)–C(14)	104.9(4)
C(18)–Fe(1)–C(20)	70.1(2)	C(12)–C(14)–C(15)	112.4(4)
C(12)–C(14)–C(21)	113.0(4)	Fe(2)–C(23)–C(24)	69.7(4)
C(15)–C(14)–C(21)	110.1(4)	C(22)–C(23)–C(24)	115.2(6)
C(14)–C(15)–C(16)	111.6(4)	Fe(2)–C(24)–C(23)	70.7(4)
C(14)–C(15)–C(20)	111.1(4)	Fe(2)–C(24)–C(25)	73.2(3)
C(16)–C(15)–C(20)	109.0(4)	C(23)–C(24)–C(25)	115.6(6)
C(15)–C(16)–C(17)	111.9(5)	Fe(2)–C(25)–C(24)	67.6(4)
Fe(1)–C(17)–C(16)	110.9(3)	Fe(2)–C(25)–C(26)	109.5(4)
C(14)–C(21)–C(22)	113.7(5)	C(24)–C(25)–C(26)	119.8(6)
C(14)–C(21)–C(26)	114.4(4)	C(21)–C(26)–C(25)	112.0(5)
C(22)–C(21)–C(26)	109.0(5)	Fe(1)–C(17)–C(18)	67.5(4)

(*continued*)

TABLE 5. (*continued*)

Fe(2)–C(22)–C(21)	109.9(4)	C(16)–C(17)–C(18)	118.5(5)
Fe(2)–C(22)–C(23)	67.9(4)	Fe(1)–C(18)–C(17)	72.5(4)
C(21)–C(22)–C(23)	120.8(5)	Fe(1)–C(18)–C(19)	70.8(4)
C(17)–C(18)–C(19)	114.7(5)	Fe(1)–C(20)–C(15)	109.5(3)
Fe(1)–C(19)–C(18)	69.4(4)	Fe(1)–C(20)–C(19)	68.2(3)
Fe(1)–C(19)–C(20)	71.8(3)	C(15)–C(20)–C(19)	121.2(5)
C(18)–C(19)–C(20)	115.0(5)	Fe(2)–C(23)–C(22)	72.1(3)

TABLE 6. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3) for **7b**

	x	y	z	U_{eq}[a]
Cr(1)	−1088(2)	2096(3)	2257(1)	52(6)
Fe(1)	3607(2)	1206(2)	1081(1)	47(5)
Fe(2)	87(2)	7073(2)	903(1)	54(5)
C(1)	−1721(18)	1625(20)	2861(9)	91(7)
O(1)	−2058(13)	1286(15)	3277(7)	120(5)
C(2)	−1350(16)	459(20)	2007(8)	78(6)
O(2)	−1520(12)	−595(15)	1896(6)	109(5)
C(3)	209(17)	1541(18)	2579(8)	77(6)
O(3)	1025(13)	1161(15)	2815(6)	113(5)
C(4)	−2459(16)	2624(17)	1967(8)	71(6)
O(4)	−3332(12)	2978(14)	1808(6)	102(5)
C(5)	−892(14)	3724(19)	2545(7)	66(5)
O(5)	−786(11)	4727(14)	2723(6)	92(4)
C(6)	3228(15)	470(18)	460(8)	70(6)
O(6)	2941(11)	−61(14)	56(6)	104(5)
C(7)	4987(16)	817(16)	1042(7)	64(6)
O(7)	5908(12)	578(13)	1033(6)	93(4)
C(8)	3256(14)	81(16)	1534(7)	56(5)
O(8)	2984(11)	−647(12)	1861(6)	82(4)
C(9)	636(15)	6355(18)	354(8)	68(5)
O(9)	1052(11)	5894(12)	−3(6)	86(4)
C(10)	−1278(16)	7192(18)	654(8)	73(6)
O(10)	−2213(14)	7283(15)	508(6)	116(5)
C(11)	384(17)	8660(21)	780(8)	85(6)
O(11)	540(13)	9735(17)	687(7)	126(6)
C(12)	−275(11)	2618(13)	1613(6)	37(4)
O(12)	−4748(8)	2434(9)	1087(4)	50(3)
C(13)	−1434(13)	1768(15)	863(7)	61(5)
C(14)	805(12)	3361(13)	1673(6)	39(4)
C(15)	1757(11)	2351(13)	1609(5)	32(4)
C(16)	2785(11)	2618(14)	1996(6)	45(5)
C(17)	3837(13)	2513(13)	1734(6)	45(5)
C(18)	3900(13)	3096(15)	1236(6)	51(5)
C(19)	2999(12)	2926(15)	855(7)	54(5)
C(20)	2107(12)	2243(14)	1042(6)	43(4)
C(21)	830(11)	4504(13)	1275(6)	40(4)
C(22)	−185(13)	5311(14)	1292(6)	46(4)
C(23)	−240(14)	6387(16)	1648(7)	60(5)
C(24)	672(14)	7156(18)	1701(7)	63(5)
C(25)	1545(14)	6760(16)	1411(7)	61(5)
C(26)	1852(13)	5354(15)	1397(7)	59(5)
C(27)	124(28)	2088(33)	4660(13)	200(2)
Cl(1)	10896(10)	1282(13)	5128(15)	250(4)
Cl(2)	454(11)	2141(14)	4059(5)	260(4)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 7. Selected bond lengths (Å) and angles (°) for **7b**

Bond distances (Å)			
Cr(1)–C(1)	1.809(23)	Cr(1)–C(2)	1.850(21)
Cr(1)–C(3)	1.815(20)	Cr(1)–C(4)	1.858(19)
Cr(1)–C(5)	1.864(20)	Cr(1)–C(12)	2.022(15)
Fe(1)–C(6)	1.753(19)	Fe(1)–C(7)	1.749(19)
Fe(1)–C(8)	1.710(17)	Fe(1)–C(17)	2.126(15)
Fe(1)–C(18)	2.052(16)	Fe(1)–C(19)	2.019(16)
Fe(1)–C(20)	2.131(15)	Fe(2)–C(9)	1.737(20)
Fe(2)–C(10)	1.739(20)	Fe(2)–C(11)	1.742(22)
Fe(2)–C(22)	2.128(16)	Fe(2)–C(23)	2.050(17)
Fe(2)–C(24)	2.050(17)	Fe(2)–C(25)	2.127(17)
C(12)–O(12)	1.321(17)	O(12)–C(13)	1.440(19)
C(12)–C(14)	1.533(19)	C(14)–C(15)	1.594(19)
C(14)–C(21)	1.557(20)	C(15)–C(16)	1.546(19)
C(16)–C(17)	1.492(21)	C(17)–C(18)	1.386(22)
C(18)–C(19)	1.404(21)	C(19)–C(20)	1.416(22)
C(20)–C(15)	1.505(20)	C(21)–C(22)	1.508(21)
C(22)–C(23)	1.441(22)	C(23)–C(24)	1.377(24)
C(24)–C(25)	1.398(25)	C(25)–C(26)	1.529(23)
C(21)–C(26)	1.549(21)		
Bond angles (°)			
C(1)–Cr(1)–C(2)	87.0(9)	C(4)–Cr(1)–C(2)	91.2(8)
C(1)–Cr(1)–C(3)	88.0(9)	C(3)–Cr(1)–C(4)	176.1(9)
C(3)–Cr(1)–C(2)	88.3(9)	C(1)–Cr(1)–C(5)	89.2(9)
C(1)–Cr(1)–C(4)	88.2(9)	C(2)–Cr(1)–C(5)	176.0(9)
C(3)–Cr(1)–C(5)	92.6(8)	C(19)–Fe(1)–C(20)	69.8(6)
C(4)–Cr(1)–C(5)	87.6(8)	C(9)–Fe(2)–C(10)	100.0(9)
C(1)–Cr(1)–C(12)	175.9(8)	C(9)–Fe(2)–C(11)	100.4(9)
C(2)–Cr(1)–C(12)	94.1(8)	C(10)–Fe(2)–C(11)	94.4(9)
C(3)–Cr(1)–C(12)	88.1(8)	C(9)–Fe(2)–C(22)	93.4(8)
C(4)–Cr(1)–C(12)	95.7(8)	C(10)–Fe(2)–C(22)	92.5(8)
C(5)–Cr(1)–C(12)	89.8(7)	C(11)–Fe(2)–C(22)	163.3(8)
C(6)–Fe(1)–C(7)	92.1(9)	C(9)–Fe(2)–C(23)	131.8(8)
C(6)–Fe(1)–C(8)	102.0(9)	C(10)–Fe(2)–C(23)	95.4(8)
C(7)–Fe(1)–C(8)	99.7(8)	C(11)–Fe(2)–C(23)	123.7(8)
C(6)–Fe(1)–C(17)	164.7(8)	C(22)–Fe(2)–C(23)	40.3(6)
C(7)–Fe(1)–C(17)	97.1(8)	C(9)–Fe(2)–C(24)	130.2(8)
C(8)–Fe(1)–C(17)	88.5(7)	C(10)–Fe(2)–C(24)	126.3(8)
C(6)–Fe(1)–C(18)	128.6(8)	C(11)–Fe(2)–C(24)	93.8(8)
C(7)–Fe(1)–C(18)	94.7(7)	C(22)–Fe(2)–C(24)	69.9(7)
C(8)–Fe(1)–C(18)	126.7(7)	C(23)–Fe(2)–C(24)	39.3(7)
C(17)–Fe(1)–C(18)	38.7(6)	C(9)–Fe(2)–C(25)	92.1(8)
C(6)–Fe(1)–C(19)	95.0(8)	C(10)–Fe(2)–C(25)	163.6(8)
C(7)–Fe(1)–C(19)	122.1(8)	C(11)–Fe(2)–C(25)	94.3(8)
C(8)–Fe(1)–C(19)	134.2(8)	C(22)–Fe(2)–C(25)	75.6(6)
C(17)–Fe(1)–C(19)	69.8(6)	C(23)–Fe(2)–C(25)	68.1(7)
C(18)–Fe(1)–C(19)	40.3(6)	C(24)–Fe(2)–C(25)	39.0(7)
C(6)–Fe(1)–C(20)	91.1(8)	C(12)–O(12)–C(13)	122.2(12)
C(7)–Fe(1)–C(20)	161.8(7)	Cr(1)–C(12)–O(12)	132.4(10)
C(8)–Fe(1)–C(20)	97.1(7)	Cr(1)–C(12)–C(14)	122.5(10)
C(17)–Fe(1)–C(20)	76.4(6)	O(12)–C(12)–C(14)	105.1(12)
C(18)–Fe(1)–C(20)	69.5(6)	C(12)–C(14)–C(15)	106.4(10)
C(12)–C(14)–C(21)	113.1(11)	Fe(2)–C(23)–C(24)	70.4(10)
C(15)–C(14)–C(21)	113.7(12)	C(22)–C(23)–C(24)	116.3(15)
C(14)–C(15)–C(16)	112.5(11)	Fe(2)–C(24)–C(23)	70.4(10)
C(14)–C(15)–C(20)	114.1(11)	Fe(2)–C(24)–C(25)	73.5(10)
C(16)–C(15)–C(20)	108.4(11)	C(23)–C(24)–C(25)	115.0(16)
C(15)–C(16)–C(17)	113.8(12)	Fe(2)–C(25)–C(24)	67.5(9)
Fe(1)–C(17)–C(16)	108.2(10)	Fe(2)–C(25)–C(26)	109.4(11)
C(14)–C(21)–C(22)	111.2(12)	C(24)–C(25)–C(26)	120.0(15)
C(14)–C(21)–C(26)	112.3(12)	C(21)–C(26)–C(25)	111.6(13)
C(22)–C(21)–C(26)	108.9(12)	Fe(1)–C(17)–C(18)	67.7(9)

(*continued*)

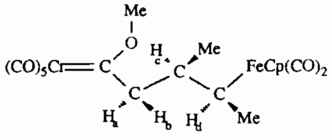
TABLE 7. (*continued*)

Fe(2)–C(22)–C(21)	108.7(10)	C(16)–C(17)–C(18)	117.8(13)
Fe(2)–C(22)–C(23)	66.9(9)	Fe(1)–C(18)–C(17)	73.6(9)
C(21)–C(22)–C(23)	122.5(13)	Fe(1)–C(18)–C(19)	68.6(9)
C(17)–C(18)–C(19)	116.5(15)	Fe(1)–C(20)–C(15)	107.7(9)
Fe(1)–C(19)–C(18)	71.1(9)	Fe(1)–C(20)–C(19)	65.9(9)
Fe(1)–C(19)–C(20)	74.4(9)	C(15)–C(20)–C(19)	123.4(13)
C(18)–C(19)–C(20)	115.5(14)	Fe(2)–C(23)–C(22)	72.8(9)

(–CH$_2$CH(Me)CH(CH_3)). MS (EI): *m*/*z* 453 (M^+ – CO).

*Addition of **2** to [Cp(CO)$_2$Fe(η^2-trans-2-butene)]$^+$BF$_4^-$ to form complex **4***

This compound was prepared similarly to **3** using **1** (0.55 g, 2.2 mmol), n-BuLi (1.56 ml of a 1.6 M solution in hexanes, 2.3 mmol) and [Cp(CO)$_2$Fe(η^2-*trans*-2-butene)]BF$_4$ (0.65 g, 2.2 mmol). Chromatography and isolation as above for **3** gave **4** as a yellow solid in 37% yield (0.39 g, 0.81 mmol).

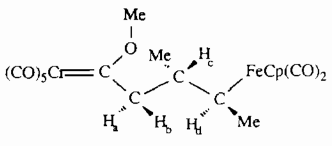


4

4: IR (CH$_2$Cl$_2$): ν(CO) = 2055(w), 1995(m), 1935(vs) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.10 (s, 8H, OCH_3 + Cp), 3.48 (ABX pattern, 2H, H_aH_b, *J*(HaHb) = 14.7 Hz, *J*(HaHc) = 8.7 Hz, *J*(HbHc) = 3.5 Hz), 2.41 (dq, 1H, H_d, *J*(HdHc) = 5.7 Hz, *J*(HdH(Me)) = 7.1 Hz), 2.25 (m, 1H, H_c), 1.31 (d, 3H, CH_3, *J*(HdH(Me)) = 7.1 Hz), 0.96 (d, 3H, CH_3, *J*(HcH(Me)) = 6.7 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 366.5 (Cr=*C*), 224.3 (*trans*-Cr–*C*O), 218.7, 218.5 (Fe–*C*O), 217.1 (*cis*-Cr–*C*O), 86.7 (C_5H_5), 69.8 (Cr=C(OMe)*C*H$_2$), 68.3 (O*C*H$_3$), 44.8 (–CH$_2$*C*H(Me)), 27.4 (CH$_2$CH(Me)*C*H(Me)), 26.8 (CH$_2$CH(*C*H$_3$), 21.9 (CH$_2$CH(Me)CH(*C*H$_3$)). MS (EI): *m*/*z* = 453 (M^+ – CO).

*Addition of **2** to [Cp(CO)$_2$Fe-(η^2-styrene)]$^+$BF$_4^-$ to form complex **5***

This compound was prepared similarly to **3** using **1** (0.55 g, 2.2 mmol), n-BuLi (1.56 ml of a 1.6 M solution in hexanes, 2.3 mmol) and [Cp(CO)$_2$Fe(η^2-styrene)]BF$_4$ (0.76 g, 2.2 mmol). Chromatography and isolation as above for **3** gave **5** in 49% yield as a yellow solid (0.57 g, 1.1 mmol).

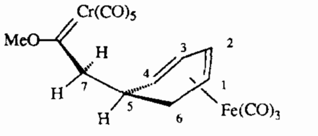


5

5: IR (CH$_2$Cl$_2$): ν(CO) = 2055(w), 1995(m), 1935(vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.15–6.80 (m, 5H, Ph), 4.52 (s, 5H, Cp), 4.48 (s, 3H, OCH_3), 3.66 (ABX pattern, 2H, H_aH_b, *J*(HaHb) = 14.9 Hz, *J*(HaHc) = 5.9 Hz, *J*(HbHc) = 8.4 Hz), 3.07 (m, 1H, H_c), 1.67 (ABX pattern, 2H, H_dH_e, *J*(HdHc) = 10.1 Hz, *J*(HdHe) = 10.1 Hz, *J*(HcHe) = 3.5 Hz). ^{13}C NMR (CDCl$_3$): δ 362.3 (Cr=*C*), 223.8 (*trans*-Cr–CO), 217.3, 217.2 (Fe–*C*O), 216.8 (*cis*-Cr–*C*O), 146.8, 128.5, 127.9, 126.5 (Ph), 85.7 (C_5H_5), 74.7 (Cr=C(OMe)*C*H$_2$), 67.9 (O*C*H$_3$), 50.8 (–CH$_2$*C*H(Ph)), 9.6 (CH$_2$CH(Ph)*C*H$_2$). MS (EI): *m*/*z* = 361 (M^+ – 6CO).

*Addition of **2** to [(η^5-cyclohexadienyl)Fe(CO)$_3$]$^+$BF$_4^-$ to form complex **6***

The chromium carbene anion complex **2** was generated *in situ* in THF (15 ml) from **1** (0.50 g, 2.0 mmol) and n-BuLi (1.4 ml of a 1.6 M solution in hexanes, 2.3 mmol). [(η^5-cyclohexadienyl)-Fe(CO)$_3$]$^+$BF$_4^-$ (0.67 g, 2.2 mmol) was added to the –50 °C solution to induce an immediate color change from yellow to orange. The solution was stirred for 12 h while slowly warming to room temperature. The THF was removed under vacuum to afford an orange oil which was purified by column chromatography on neutral alumina. Elution with 1:1 CH$_2$Cl$_2$/pentane afforded a yellow band of **6** which was obtained as an orange oil upon solvent evaporation (0.91 g, 1.9 mmol, 97%). Crystals suitable for X-ray diffraction analysis were grown from benzene/petroleum ether.

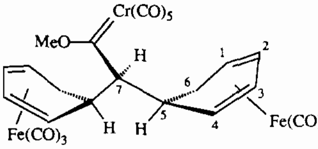


6

6: *Anal.* Calc. for C$_{17}$H$_{12}$CrFeO$_9$: C, 43.62; H, 2.58. Found: C, 44.90; H, 2.90%. IR (CH$_2$Cl$_2$): ν(CO) = 2055(w), 2037(m), 1960(s), 1937(s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.41 (m, H_2, *J*(H2H3) = 4.2 Hz), 5.33 (m, H_3, *J*(H3H2) = 4.2 Hz), 4.79 (s, 3H, OCH_3), 3.33 (ABX pattern, $H_7H_{7\prime}$, *J*(H7H7′) = 16.1 Hz, *J*(H7H5) = 7.9 Hz, *J*(H7′H5) = 6.4 Hz), 3.04 (dddd, H_1, *J*(H1H2) = 6.2 Hz, *J*(H1H3) = 2.2 Hz, *J*(H1H6) = 3.9 Hz, *J*(H1H6′) = 2.2 Hz), 2.99 (dddd, H_4, *J*(H4H2) = 1.5 Hz, *J*(H4H3) = 6.3 Hz, *J*(H4H5) = 3.5 Hz), 2.61 (m, H_5), 1.95 (ddd, *endo*-H_6, *J*(H6H6′) = 15.0 Hz, *J*(H6H1) = 3.9 Hz, *J*(H6H5) = 10.5 Hz), 1.16 (dddd, *exo*-$H_{6\prime}$, *J*(H6′H1) = 2.2 Hz, *J*(H6′H2) = 1.1 Hz, *J*(H6′H5) = 3.3 Hz, *J*(H6′H6) = 15.0 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 361.9 (Cr=*C*), 223.8 (*trans*-Cr–*C*O), 216.9 (*cis*-Cr–*C*O), 212.4 (Fe–*C*O), 86.5, 85.1 (C_2 and C_3), 73.3 (C_7), 68.5 (O*C*H$_3$), 66.0, 60.3 (C_1 and C_4), 35.9 (C_5), 30.8 (C_6). MS (FAB): *m*/*z* = 468 (M^+).

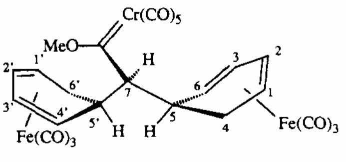
Addition of $Li[(CO)_5Cr{=}C(OMe)CH\{(\eta^5\text{-cyclohexadienyl})Fe(CO)_3\}]$ *to* $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3][BF_4]$ *to form 7*

The chromium carbene anion complex $Li[(CO)_5Cr{=}C(OMe)CH\{(\eta^5\text{-cyclohexadienyl})Fe(CO)_3\}]$ was generated *in situ* by addition of $^{n}BuLi$ (0.312 ml of a 1.6 M solution in hexanes, 0.5 mmol) to a solution of **6** (~0.5 mmol, prepared *in situ* as described above starting from 0.125 g (0.5 mmol) of **1**, 0.312 ml of a 1.6 M solution of $^{n}BuLi$ in hexanes (0.5 mmol) and 0.153 g of $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3][BF_4]$ (0.5 mmol)) in 5 ml of THF at −78 °C. After stirring for 15 min, $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3][BF_4]$ (0.153 g, 0.5 mmol) was added to the −78 °C solution. The solution was stirred for 4 h while slowly warming to room temperature. The THF was removed under vacuum to afford an orange oil which was purified by column chromatography on neutral alumina. Elution with 1:1 Et_2O/pentane afforded a yellow band of **7** which was obtained as an orange microcrystalline powder upon solvent evaporation (0.250 g, 73%). At this stage, a ^{13}C NMR spectrum clearly showed the presence of two isomers **7a** and **7b** in an approximate 1:1 ratio. A recrystallization of the compound in a mixture of benzene and petroleum ether (1:3) at room temperature gave two types of crystals which were easily sorted. Crystals of **7a** and **7b** suitable for X-ray diffraction analyses were respectively grown from benzene/petroleum ether (1:3) at room temperature and from CH_2Cl_2 at −20 °C.



7a

7a: *Anal.* Calc. for $C_{26}H_{18}CrFe_2O_{12}$: C, 45.52; H, 2.64. Found: C, 45.49; H, 2.38%. IR (CH_2Cl_2): ν(CO) = 2055(w), 2037(m), 1960(s), 1937(s) (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.39 (m, H_2, *J*(H2H3) = 4.2 Hz), 5.28 (m, H_3, *J*(H3H2) = 4.2 Hz), 4.82 (s, 3H, OCH_3), 3.81 (t, H_7, *J*(H7H5) = 6.2 Hz), 3.10 (dddd, H_1, *J*(H1H2) = 5.9 Hz, *J*(H1H3) = 1.4 Hz, *J*(H1H6) = 4.2 Hz, *J*(H1H6′) = 1.9 Hz), 2.86 (ddd, H_4, *J*(H4H2) = 1.8 Hz, *J*(*H4H3*) = 6.2 *Hz*, *J*(H4H5) = 3.5 Hz), 2.39 (m, H_5), 1.83–1.43 (m, *endo*-H_6 and *exo*-$H_{6'}$, *J*(H6H6′) = 14.8 Hz, *J*(H6H1) = 4.2 Hz, *J*(H6H5) = 10.5 Hz, *J*(H6′H1) = 1.9 Hz, *J*(H6′H2) = 1.0 Hz, *J*(H6′H5) = 5.1 Hz). ^{13}C NMR ($CDCl_3$): δ 361.0 (Cr=*C*), 223.8 (*trans*-Cr–*C*O), 216.6 (*cis*-Cr–*C*O), 212.0 (Fe–*C*O), 86.7, 85.2 (C_2 and C_3), 84.5 (C_7), 68.2 (OCH_3), 64.5, 59.1 (C_1 and C_4), 40.5 (C_5), 28.3 (C_6). MS (FAB): *m/z* = 686 (M^+).



7b

7b: *Anal.* Calc. for $C_{26}H_{18}CrFe_2O_{12}$: C, 45.52; H, 2.64. Found: C, 45.50; H, 2.46%. IR (CH_2Cl_2): ν(CO) = 2055(w), 2037(m), 1960(s), 1937(s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.45–5.28 (m, H_2, H_3, $H_{2'}$, $H_{3'}$), 4.83 (s, 3H, OCH_3), 3.77 (dd, H_7, *J*(H7H5) = 8.2 Hz, *J*(H7H5′) = 4.6 Hz), 3.15–3.01 (m, H_1, $H_{1'}$, $H_{4'}$), 2.86 (ddd, H_4, *J*(H4H2) = 1.2 Hz, *J*(H4H3) = 6.0 Hz, *J*(H4H5) = 2.9 Hz), 2.50 (dddd, H_5, *J*(H5H4) = 3.2 Hz, *J*(H5H6a) = 10.4 Hz, *J*(H5H6b) = 4.7 Hz, *J*(H5H7) = 8.2 Hz), 2.23 (dddd, $H_{5'}$, *J*(H5′H4′) = 3.6 Hz, *J*(H5′H6′a) = 11.1 Hz, *J*(H5′H6′b) = 3.6 Hz, *J*(H5′H7) = 4.6 Hz), 1.96 (ddd, *endo*-$H_{6'a}$, *J*(H6′aH6′b) = 15.3 Hz, *J*(H6′aH5′) = 11.1 Hz, *J*(H6′aH1′) = 3.7 Hz), 1.89 (ddd, *endo*-H_{6a}, *J*(H6aH6b) = 15.0 Hz, *J*(H6aH5) = 10.4 Hz, *J*(H6aH1) = 3.7 Hz), 1.48 (dddd, *exo*-$H_{6'b}$, *J*(H6′bH1′) = 2.3 Hz, *J*(H6′bH2′) = 1.1 Hz, *J*(H6′bH5′) = 3.7 Hz, *J*(H6′bH6′a) = 15.3 Hz), 1.32 (dddd, *exo*-H_{6b}, *J*(H6bH1) = 2.1 Hz, *J*(H6bH2) = 1.1 Hz, *J*(H6bH5) = 4.7 Hz, *J*(H6bH6a) = 15.0 Hz). ^{13}C NMR ($CDCl_3$): δ 361.0 (Cr=*C*), 223.0 (*trans*-Cr–*C*O), 216. 6 (*cis*-Cr–*C*O), 212.0 (Fe–*C*O), 86.7, 86.1, 85.4, 85.2 (C_2, C_3, $C_{2'}$, $C_{3'}$), 83.1 (C_7), 68.3 (OCH_3), 64.6, 62.6, 59.6, 59.2 (C_1, C_4, $C_{1'}$, $C_{4'}$), 41.1, 39.7 (C_5, $C_{5'}$), 29.7, 28.5 (C_6, $C_{6'}$). MS (FAB): *m/z* = 686 (M^+).

Crystallographic characterization of 6, 7a and 7b·CH$_2$Cl$_2$

Crystal, data collection and refinement parameters are collected in Table 1. Yellow crystals of **6** and **7a** were each mounted on fine glass fibers with epoxy cement and the data were collected at the University of Delaware. The unit-cell parameters of both were determined from the least-squares fit of 25 reflections ($20 \leqslant 2\theta \leqslant 25°$). Preliminary photographic characterizations showed 2/*m* and $\bar{1}$ Laue symmetry for **6** and **7a**, respectively. No correction for absorption was applied. During data collection, **6** experienced a ~35% decrease in the check reflection intensities; a linear correction was applied to the data, but the overall quality of this structure is probably a result of the inadequacies of a single correction throughout the entire range of 2θ. All processing of the data for **7a** was confined to the centrosymmetric space group, $P\bar{1}$, which provided the chemically reasonable structure reported. **6** and **7a** were both solved by direct methods which located the Fe and Cr atoms. The remaining non-hydrogen atoms were all located through subsequent least-squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (dCC = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms for **7a** were refined with anisotropic thermal parameters. For **6**, only the non-hydrogen and non-carbon atoms were refined with anisotropic thermal parameters due to the loss of data from the decay during the data collection. Tables 2 and 3 contain positional parameters for **6** and **7a** respectively, and Tables 4 and 5 contain relevant bond distances and bond angles for **6** and **7a**, respectively. All computer programs and the sources of the scattering factors are contained in the SHELXTLPLUS program library (4.11) (G. Sheldrick; Siemens, Madison, WI).

In order to minimize the crystal decomposition, probably due to the loss of crystallization solvent, the selected crystal of **7b** was sealed in a capillary tube in a mixture of paraffin oil and dichloromethane (1:1). Data for **7b** were collected in Toulouse, and cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $10 < 2\theta(\text{Mo K}\alpha_1) < 12°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. Data reductions were carried out using the SDP crystallographic computing package [13a]. The monitoring of three reflections every 2 h, showed a loss of 31% in intensity during the data collection. A linear decay correction was applied. Table 1 presents further crystallographic information. The position of Fe and Cr atoms was determined by direct methods by using the SHELXS package [13b]. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELX package [13c]. A molecule of solvent, CH_2Cl_2, for each molecule of **7b** was found in the crystal lattice. Atomic scattering factors were taken from the usual tabulations [13d]. Anomalous dispersion terms for Fe, Cr and Cl atoms were included in F_c [13e]. Empirical absorption correction was applied [13f]. Fe, Cr and Cl atoms were allowed to vibrate anisotropically. Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart *et al.* [13g].

Supplementary material

Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, hydrogen atom positions, and structure factors for **6**, **7a** and **7b** are available from G.L.G. upon request.

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References

1 (a) C. P. Casey and R. L. Anderson, *J. Am. Chem. Soc.*, *96* (1974) 1230; (b) *J. Organomet. Chem.*, *73* (1974) C28; (c) C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, *102* (1975) 175; (d) *Inorg. Chem.*, *16* (1977) 391; (e) C. P. Casey, W. R. Brunsvold and D. M. Scheck, *Inorg. Chem.*, *16* (1977) 3059; (f) C. P. Casey, *Chemtech*, (1979) 379; (g) C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, *118* (1976) 309; (h) M. Rudler-Chauvin and H. Rudler, *J. Organomet. Chem.*, *212* (1981) 203; (i) C. Alverez-Toledano, A. Parlier, F. Rose-Munch, H. Rudler, J. C. Daran, C. Knobler and Y. Jeannin, *J. Organomet. Chem.*, *323* (1987) 371; (j) Y. C. Xu and W. D. Wulff, *J. Org. Chem.*, *52* (1987) 3263; (k) D. W. Macomber, P. Madhukar and R. D. Rogers, *Organometallics*, *8* (1989) 1275.

2 C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, *77* (1974) 345.

3 (a) C. Kelley, N. Lugan, M. R. Terry, G. L. Geoffroy and A. L. Rheingold, *J. Am. Chem. Soc.*, in press; (b) C. Kelley, *Ph. D. Dissertation*, The Pennsylvania State University, 1991.

4 (a) D. W. Macomber, M. Hung, M. Puttannachetty, M. Liang and R. D. Rogers, *Organometalllics*, *10* (1991) 737; (b) D. W. Macomber, M. H. Hung, A. G. Verma and R. D. Rodgers, *Organometallics*, *7* (1988) 2072.

5 J. Breimair, T. Weidmann, B. Wagner and W. Beck, *Chem. Ber.*, *124* (1991) 2431; B. Niemer, J. Breimair, B. Wagner, K. Polborn and W. Beck, *Chem. Ber.*, *124* (1991) 2227.

6 (a) P. M. Lennon, A. M. Rosan and M. Rosenblum, *J. Am. Chem. Soc.*, *99* (1977) 8426; (b) T. C. T. Cheng and M. Rosenblum, *J. Org. Chem.*, *46* (1981) 4103; (c) M. Marsi and M. Rosenblum, *J. Am. Chem. Soc.*, *106* (1984) 7264; (d) M. Rosenblum, *Acc. Chem. Res.*, *7* (1974) 122.

7 (a) L. S. Hegedus, in F. R. Hartly (ed.), *The Chemistry of the Metal–Carbon Bond*, Vol. 2, Wiley–Interscience, New York, 1985, pp. 482–489; (b) A. J. Pearson, *Acc. Chem. Res.*, *13* (1980) 463; (c) S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron*, *34* (1978) 3047; (d) S. G. Davies, M. L. H. Green and D. M. P. Mingos, in P. S. Bratterman (ed.), *Reactions of Coordinated Ligands*, Vol. 1, Plenum, New York, 1986, pp. 897–938.

8 U. Schubert, in *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, pp. 74–111.

9 (a) F. A. Cotton and J. M. Group, *J. Organomet. Chem.*, *77* (1974) 369; (b) B. F. G. Johnson, J. Lewis, D. G. Parker, P. R. Raithby and G. M. Sheldrick, *J. Organomet. Chem.*, *150* (1978) 115.

10 E. O. Fischer and A. Maasböl, *Chem. Ber.*, *100* (1967) 2445.

11 (a) W. P. Giering, M. Rosenblum and J. Tancrede, *J. Am. Chem. Soc.*, *94* (1972) 7170; (b) D. L. Reger and C. Coleman, *J. Organomet. Chem.*, *131* (1977) 153.

12 E. O. Fischer and R. D. Fischer, *Angew. Chem.*, *23* (1960) 919.

13 (a) *Enraf-Nonius Structure Determination Package,* B. A. Frenz & Associates, Inc. College Station, TX, Enraf-Nonius, Delft, Netherlands, 4th edn., 1981; (b) G. M. Sheldrick, *SHELXS-86,* program for crystal structure solution, University of Göttingen, Göttingen, FRG, 1986; (c) G. M. Sheldrick, *SHELX-76,* program for crystal structure determination, University of Cambridge, Cambridge, UK, 1976; (d) D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974, Table 2.2B; (e) Table 2.3.1; (f) N. Walker and D. I. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158; (g) R. E. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42* (1965) 3175.