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Facile conversion of (η^5-C_5R_5)M(CO)$_2$–halide complexes to halomethyl, alkoxymethyl, and cyanomethyl derivatives (R = H, CH_3; M = Fe, Ru; halide = Cl, Br, I)

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Abstract

The CpM(CO)$_2$–X complexes (M = Fe, Ru; X = Cl, Br; Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) are completely converted to the corresponding halomethyl derivatives over a 20–30 min period when ethereal diazomethane is added dropwise in the presence of Cu powder. Product work-up involves only simple extraction of the crude product with hexane followed by recrystallization at −40°C. Formation of iodomethyl derivatives from iodide precursors requires considerably longer CH_2N_2 addition times and cannot be completely freed of the starting iodide complexes. Fortunately, iodomethyl complexes can be prepared in 80–95% isolated yield by treating the chloromethyl or bromomethyl derivatives with NaI in acetone/Et_2O. The CpFe(CO)$_2$CH$_2$I and Cp*Fe(CO)$_2$CH$_2$I complexes are the most sensitive, decomposing rapidly to polymethylene and the parent iodide complexes upon standing at room temperature. Metathetical reactions of the halomethyl complexes to give alkoxymethyl and cyanomethyl derivatives are described.

Introduction

Over the past several years we have reported the reactivity of selected organometallic (halo)nitrosyl complexes with diazomethane and Cu powder to produce the novel halomethyl derivatives (eqs. 1 and 2) [1,2].

$$\mathrm{CpCr(NO)_2X} \xrightarrow{\mathrm{CH_2N_2/Cu/Et_2O}} \mathrm{CpCr(NO)_2CH_2X} \qquad (1)$$

$$\mathrm{Cp^*Ru(NO)Cl_2} \xrightarrow{\mathrm{CH_2N_2/Cu/Et_2O}} \mathrm{Cp^*Ru(NO)(CH_2Cl)Cl} \xrightarrow{\mathrm{CH_2N_2/Cu/Et_2O}} \mathrm{Cp^*Ru(NO)(CH_2Cl)_2} \qquad (2)$$

$(\mathrm{Cp} = \eta^5\text{-}C_5H_5;\ \mathrm{Cp^*} = \eta^5\text{-}C_5Me_5;\ X = \mathrm{Cl, Br, I})$

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One of our principal goals in this work has been to compare the chemistry of our new nitrosyl complexes with the chemistry reported for isoelectronic metal–carbonyl complexes [3]. Now we report that our CH_2N_2/Cu conditions are also successful for producing a wide variety of $(\eta^5\text{-}C_5R_5)M(CO)_2$–halomethyl complexes ($M = Fe$, Ru; $R = H$, CH_3). Although a number of these complexes are known from other synthetic routes [3,4], the methods presented here provide easy access to these complexes without the need for generating the $CpM(CO)_2^-$ anions or the use of chloromethyl alkyl ethers. Similar to the report by Flood *et al.* [5] we show that lability of the halomethyl halide substituent provides easy access to new iodomethyl complexes $CpM(CO)_2CH_2I$ as well as to alkoxymethyl and cyanomethyl derivatives. For the sake of completeness, we provide here a compilation of ^1H and ^{13}C NMR, IR, and mass spectroscopy data for all of the compounds.

Results and discussion

Synthesis of halomethyl complexes

The formation of chloromethyl and bromomethyl derivatives of the $CpM(CO)_2X$ precursors follows from the same conditions reported for the formation of the $CpCr(NO)_2CH_2X$ complexes (eq. 3) [1].

$$CpM(CO)_2X \xrightarrow{CH_2N_2/Cu/Et_2O} CpM(CO)_2CH_2X \quad (3)$$

$(Cp = \eta^5\text{-}C_5H_5,\ \eta^5\text{-}C_5Me_5;\ M = Fe, Ru;\ X = Cl, Br, I)$

Typical is the conversion of $CpFe(CO)_2Cl$ to $CpFe(CO)_2CH_2Cl$, which is easy to detect visually as well as by solution IR. The reaction mixture changes from red to light yellow over the time of CH_2N_2 addition. After the starting complex is no longer detectable by solution IR, the mixture is filtered to remove the Cu powder and taken to dryness *in vacuo*. The product is easily isolated by single extraction of the residue with hexane followed by filtration and crystallization from the concentrated hexane extract at −40°C.

In contrast to previous routes to the $CpM(CO)_2CH_2X$ complexes [3,4], the CH_2N_2/Cu method has the advantage of eliminating the need for generating $CpM(CO)_2^-$ anions. Our method still requires care in handling diazomethane, but we have found that peristaltic pumping of the ethereal solution through Teflon cannula and Viton rubber is safe and convenient. An alternative to peristaltic pumping is simply to siphon the CH_2N_2 solution through Teflon cannula into the reaction vessel. Qualitatively, we have observed the rate of halomethyl product formation to be slowed when large amounts of polymeric $-(CH_2)_x-$ are present in the reaction mixture. Thus, care must be taken to avoid adding the CH_2N_2 solution too quickly.

Compared with the reactivity of the metal chloride and bromide complexes with CH_2N_2/Cu, the metal iodide complexes can be converted to the iodomethyl derivatives in only moderate yields and are difficult to separate from the parent iodide complexes. Fortunately, treatment of the corresponding Ru–chloromethyl complexes with excess of NaI in acetone/Et_2O gives rapid conversion to the iodomethyl complexes (eq. 4).

$$CpM(CO)_2CH_2X + NaI \xrightarrow{Et_2O/acetone} CpM(CO)_2CH_2I + NaX \quad (4)$$

$(X = Cl, Br;\ M = Fe, Ru)$

The $CpFe(CO)_2CH_2I$ and $Cp^\star Fe(CO)_2CH_2I$ complexes are the most unstable of all halomethyl complexes we have prepared, decomposing within several hours at room temperature to the parent iodo complexes and polymethylene. Other reports have also commented on the instability of iodomethyl complexes [4b,5]. The intermediacy of these complexes has been suggested in the formation of $(\eta^5\text{-}C_5R_5)Fe(CO)_2CH_2PR_3^+$ complexes [4c]. It is interesting that when monitored by ^1H NMR, $CDCl_3$ solutions of $CpFe(CO)_2CH_2I$ and $Cp^\star Fe(CO)_2CH_2I$ that contain added [PPN]I decompose more slowly than those containing no added iodide. This would be consistent with the added iodide suppressing "ionization" of the $M\text{-}CH_2\text{-}I$ group to an $M{=}CH_2^+I^-$ form. The Ru-iodomethyl complexes are considerably more stable than their Fe analogues.

Spectroscopic properties of the halomethyl complexes

The NMR and IR spectral features of the halomethyl complexes are summarized in Table 1. In the ^1H NMR spectrum the complexes show a single resonance for the Cp or $Cp^\star$ ligand protons. The singlet for the halomethyl methylene protons shift steadily to higher field as X varies $Cl \rightarrow Br \rightarrow I$. In the ^{13}C NMR spectrum, the resonances for the Cp or $Cp^\star$ and the carbonyl carbon atoms are clearly present and show no large shifts as a function of the halomethyl halide. Reflecting the shifts observed in the ^1H NMR spectra, the methylene carbon resonance shifts steadily to high field as X varies $Cl \rightarrow Br \rightarrow I$. The carbonyl absorptions in the IR for the halomethyl complexes do not vary significantly as a function of the halomethyl identity.

The mass spectral data for the halomethyl complexes are summarized in Table 2. It is quite clear that loss of the halide substituent to give the $(\eta^5\text{-}C_5R_5)M(CO)_2{=}CH_2^+$ cation is extremely favorable. Consistent with the known chemistry of $(\eta^5\text{-}C_5R_5)M(CO)_2{=}CHR^+$ methylidene complexes [4], the stability of the methylidene cations generated in the mass spectrometer is quite reasonable.

Synthesis of alkoxymethyl complexes

The halomethyl complexes can be easily converted to alkoxymethyl derivatives by either the use of thallium ethoxide or by treatment with alkoxides in alcohol (eqs. 5 and 6). Flood *et al.* [5] have shown that $CpFe(CO)(PPh_3)CH_2Cl$ can be converted to $CpFe(CO)(PPh_3)CH_2OCH_3$ by using KOAc in MeOH.

$$Cp^\star Fe(CO)_2CH_2Cl + TlOEt \xrightarrow{EtOH} Cp^\star Fe(CO)_2CH_2OEt + TlCl \qquad (5)$$

$$CpM(CO)_2CH_2X + OR^- \xrightarrow{ROH} CpM(CO)_2CH_2OR + X^- \qquad (6)$$

$M = Fe$: Cp; $R = CH_3$
$Cp^\star$; $R = CH_3, CH(CH_3)_2$
$M = Ru$: Cp; $R = CH_3$

This method of converting halomethyl complexes to alkoxymethyl derivatives avoids the use of chloromethyl ethers.

Consistent with earlier characterizations, the alkoxymethyl derivatives are light and heat sensitive oils. They can be purified by vacuum sublimation on to a dry-ice-cooled finger, giving light yellow oils that, upon exposure to room light and room temperature conditions, give brownish-yellow oils. This sensitivity has pre-

Table 1

NMR and IR data for halomethyl complexes

Compound	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)	IR, ν(CO) (cm^{-1}) [c]
$CpFe(CO)_2CH_2Cl$	4.21 (s, 2H, CH_2) [a] 4.04 (s, 5H, C_5H_5)	215.6 (CO) [a] 86.4 (C_5H_5) 33.1 (CH_2)	2018vs, 1962vs
$CpFe(CO)_2CH_2Br$	4.01 (s, 5H, C_5H_5) [a] 3.80 (s, 2H, CH_2)	215.5 (CO) [a] 86.9 (C_5H_5) 24.3 (CH_2)	2015vs, 1962vs
$CpFe(CO)_2CH_2I$	3.97 (s, 5H, C_5H_5) [a] 2.88 (s, 2H, CH_2)	215.1 (CO) [a] 85.9 (C_5H_5) -8.0 (CH_2)	2020vs, 1965vs
$Cp^*Fe(CO)_2CH_2Cl$	3.97 (s, 2H, CH_2) [a] 1.35 (s, 15H, C_5Me_5)	217.3 (CO) [a] 96.0 (C_5Me_5) 42.1 (CH_2) 8.9 (C_5Me_5)	2003vs, 1957vs
$Cp^*Fe(CO)_2CH_2Br$	3.72 (s, 2H, CH_2) [a] 1.34 (s, 15H, C_5Me_5)	217.1 (CO) [a] 96.3 (C_5Me_5) 34.7 (CH_2) 8.94 (C_5Me_5)	2003vs, 1958vs
$Cp^*Fe(CO)_2CH_2I$	2.86 (s, 2H, CH_2) [a] 1.28 (s, 15H, C_5Me_5)	217.3 (CO) [a] 96.1 (C_5Me_5) 8.8 (C_5Me_5) 4.5 (CH_2)	2007vs, 1956vs
$CpRu(CO)_2CH_2Cl$	5.35 (s, 5H, C_5H_5) [b] 4.37 (s, 2H, CH_2)	199.7 (CO) [b] 89.5 (C_5H_5) 21.6 (CH_2)	2024vs, 1960
$CpRu(CO)_2CH_2Br$	5.36 (s, 5H, C_5H_5) [b] 4.06 (s, 2H, CH_2)	199.5 (CO) [b] 29.5 (CH_2) 89.9 (C_5H_5)	2018vs, 1966vs
$CpRu(CO)_2CH_2I$	5.33 (s, 5H, C_5H_5) [b] 3.18 (s, 2H, CH_2)	200.5 (CO) [b] 90.6 (C_5H_5) -27.3 (CH_2)	2020vs, 1975vs
$Cp^*Ru(CO)_2CH_2Cl$	3.98 (s, 2H, CH_2) [b] 1.91 (s, 15H, C_5Me_5)	202.0 (CO) [b] 100.2 (C_5Me_5) 31.7 (CH_2) 9.8 (C_5Me_5)	2008vs, 1952vs
$Cp^*Ru(CO)_2CH_2Br$	3.73 (s, 2H, CH_2) [b] 1.90 (s, 15H, C_5Me_5)	202.4 (CO) [a] 100.3 (C_5Me_5) 21.1 (CH_2) 9.4 (C_5Me_5)	2009vs, 1956vs
$Cp^*Ru(CO)_2CH_2I$	2.88 (s, 2H, CH_2) [b] 1.87 (s, 15H, C_5Me_5)	201.8 (CO) [b] 100.2 (C_5Me_5) 9.7 (C_5Me_5) -11.2 (CH_2)	2006vs, 1953vs

[a] C_6D_6 solution. [b] $CDCl_3$ solution. [c] CH_2Cl_2 solution.

Table 2

Mass spectral fragmentation intensities for the halomethyl complexes

Complex	Fragment relative intensity (%)		
	$[M^+]$	$[M-X]$	$[M-CO]$
$CpFe(CO)_2CH_2Cl$	26	100	12
$CpFe(CO)_2CH_2Br$	10	100	8
$CpFe(CO)_2CH_2I$	5	30	100
$Cp^*Fe(CO)_2CH_2Cl$	2	100	16
$Cp^*Fe(CO)_2CH_2Br$	2	100	7
$Cp^*Fe(CO)_2CH_2I$	4	82	35
$CpRu(CO)_2CH_2Cl$	11	100	7
$CpRu(CO)_2CH_2Br$	17	100	4
$CpRu(CO)_2CH_2I$	2	100	8
$Cp^*Ru(CO)_2CH_2Cl$	7	100	22
$Cp^*Ru(CO)_2CH_2Br$	8	100	7
$Cp^*Ru(CO)_2CH_2I$	2	100	21

vented us from obtaining satisfactory microanalysis for $Cp^*Ru(CO)_2CH_2OMe$, $Cp^*Fe(CO)_2CH_2OMe$, $Cp^*Fe(CO)_2CH_2OEt$, and $Cp^*Fe(CO)_2CH_2O^iPr$. Spectral evidence, however, clearly establishes the identity of the alkoxymethyl complexes. As listed in Table 3, the ^1H and ^{13}C NMR data shows the presence of the (η^5-C_5R_5), CO, and $-CH_2OR$ ligands. The infrared spectra show the carbonyl region for these alkoxymethyl complexes to be somewhat more complex than expected for a simple dicarbonyl complex. Instead of a single symmetric ν(CO) and a single asymmetric ν(CO), there are at least two resolvable bands for each when examined at 2 cm^{-1} resolution in hexane. A similar structure is observed for the $CpCr(NO)_2CH_2OR$ complexes [1], and has been tentatively assigned to the presence of conformational isomers. A full analysis of this subject is currently underway [6].

The mass spectra for the alkoxymethyl derivatives consistently show a more intense molecular ion than seen for the parent halomethyl complexes. This is consistent with a stronger CH_2–OR bond. The $(\eta^5\text{-}C_5R_5)M(CO)_2{=}CH_2^+$ fragment is still present as the most intense ion in the spectrum.

Preparation of $CpFe(CO)_2CH_2CN$

Treatment of $CpFe(CO)_2CH_2Cl$ with [PPN]CN in CH_2Cl_2 at room temperature gives irreversible conversion to the cyanomethyl derivative $CpFe(CO)_2CH_2CN$ (eq. 7).

$$CpFe(CO)_2CH_2Cl + CN^- \longrightarrow CpFe(CO)_2CH_2CN + Cl^- \qquad (7)$$

This procedure can be compared with the preparation of $CpFe(CO)(PPh_3)CH_2CN$ from $CpFe(CO)(PPh_3)CH_2Cl$ and $KCN/C_6H_6/H_2O/Bu_4NBr$ [5,7]. In the ^1H NMR spectrum the methylene protons appear as a singlet at δ 0.77 ppm. The methylene carbon appears at δ -29.3 ppm in the ^{13}C NMR spectrum. The carbonyl IR absorptions are at nearly the same energy as in the halomethyl complexes, indicating the donor properties of the $-CH_2CN$ ligand to be quite similar to the halomethyl ligands.

Table 3

NMR and IR data for alkoxymethyl and cyanomethyl complexes

Compound	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)	IR, ν(CO) (cm^{-1}) [c]
$CpFe(CO)_2CH_2OCH_3$	4.85 (s, 2H, $C\mathit{H}_2$) [b] 4.79 (s, 5H, $C_5\mathit{H}_5$) 3.23 (s, 3H, $OC\mathit{H}_3$)	217.3 ($\mathit{C}O$) [a] 85.9 (C_5H_5) 65.2 ($\mathit{C}H_2$) 60.4 ($\mathit{C}H_3$)	1998vs, 1985sh, 1949vs, 1928sh
$Cp^*Fe(CO)_2CH_2OCH_3$	4.30 (s, 2H, $C\mathit{H}_2$) [b] 3.23 (s, 3H, $OC\mathit{H}_3$) 1.73 (s, 15H, $C_5\mathit{Me}_5$)	218.4 ($\mathit{C}O$) [b] 95.3 (C_5Me_5) 73.3 ($O\mathit{C}H_3$) 61.2 ($\mathit{C}H_2$) 9.2 ($C_5\mathit{Me}_5$)	2002vs, 1991vs, 1945vs, 1934vs
$Cp^*Fe(CO)_2CH_2OCH_2CH_3$	4.35 (s, 2H, ($C\mathit{H}_2$) [b] 3.32 (q, 2H, $C\mathit{H}_2CH_3$) 1.73 (s, 15H, $C_5\mathit{Me}_5$) 1.12 (t, 3H, $CH_2C\mathit{H}_3$)	219.0 ($\mathit{C}O$) [a] 95.4 (C_5Me_5) 69.6 ($\mathit{C}H_2$) 15.6 ($CH_2\mathit{C}H_3$) 9.1 ($C_5\mathit{Me}_5$)	2000vs, 1989sh, 1943vs, 1933sh
$Cp^*Fe(CO)_2CH_2O$-*i*Pr	4.27 (s, 2H, $C\mathit{H}_2$) [b] 3.36 (m, 1H, $C\mathit{H}(CH_3)_2$) 1.72 (m, 15H, $C_5\mathit{Me}_5$) 1.07 (d, 6H, $CH(C\mathit{H}_3)_2$)	218.6 ($\mathit{C}O$) [b] 95.2 (C_5Me_5) 73.3 ($\mathit{C}H(CH_3)_2$ 66.8 ($\mathit{C}H_2$) 21.9 ($CH_2\mathit{C}H_3$) 9.2 ($C_5\mathit{Me}_5$)	1999vs, 1990sh, 1940vs, 1930sh
$Cp^*Ru(CO)_2CH_2OCH_3$	4.43 (s, 2H, $C\mathit{H}_2$) [b] 3.19 (s, 3H, $OC\mathit{H}_3$) 1.88 (s, 15H, $C_5\mathit{Me}_5$)	204.0 ($\mathit{C}O$) [b] 99.7 (C_5Me_5) 65.0 ($\mathit{C}H_2$) 60.5 ($\mathit{C}H_2$) 9.7 ($C_5\mathit{Me}_5$)	2013vs, 2003vs, 1950vs, 1940vs
$CpFe(CO)_2CH_2CN$	4.01 (s, 5H, $C_5\mathit{H}_5$) [b] 0.77 (s, 2H, $C\mathit{H}_2CN$)	215.1 ($\mathit{C}O$) [b] 85.9 (C_5H_5) -29.3 ($\mathit{C}H_2CN$)	2022vs, 1966vs [d] ν(CN) 2200 [d]

[a] C_6D_6 solution. [b] $CDCl_3$ solution. [c] Hexane solution. [d] KBr pellet.

Concluding remarks

The methods described here greatly facilitate the preparation of both new and previously reported $CpM(CO)_2$-halomethyl complexes. We have taken advantage of the labile nature of the halomethyl halide substituent, leading to facile preparation of alkoxymethyl and cyanomethyl derivatives.

Experimental

Standard Schlenk techniques were employed in all syntheses. Nitrogen atmosphere was purified by passing through scavengers for water (Aquasorb, Mallinckrodt) and oxygen (Cu catalyst, Chemical Dynamics, So. Plainfield, NJ). Reagent grade solvents were purified by distillation from appropriate drying agents. The column chromatography supports used were Al_2O_3(III) (150 mesh, activity I, neutral, Aldrich, deactivated by addition of 6% H_2O), SiO_2 (60—200 mesh, Baker) and Florisil (60–100 mesh, Fisher). Both SiO_2 and Florisil supports were activated by drying under 1×10^{-5} Torr vacuum for 24 h. Routine filtrations were performed through Analytical Filter Pulp (Schliesser and Schuller). Infrared spectra were recorded on a Perkin–Elmer 1430 spectrophotometer or a Mattson Polaris FT–IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP-270 spectrometer (270 and 67.9 MHz, respectively) or a Varian XL300 spectrometer (300 and 75.4 MHz, respectively). Residual solvent peaks were used as internal standards (7.24 ppm [^{1}H] and 77.0 ppm [^{13}C] for $CDCl_3$; 7.15 ppm [^{1}H] and 128.0 ppm [^{13}C] for C_6H_6). Mass spectra were obtained with a Finnigan 4610 mass spectrometer using chemical ionization (methane) or an LKB 2091 magnetic sector instrument employing electron impact ionization. Melting points were measured with a Mel-Temp device (Laboratory Devices) in open capillaries and are uncorrected. Combustion analyses were performed by Robertson Laboratories, Inc. Madison, NJ and Atlantic Microlabs, Inc., Norcross, GA.

Diazomethane (CH_2N_2) was generated using the "alcohol free" method from Diazald (Aldrich) [8]. Caution: diazomethane is exceedingly toxic and solutions have been known to explode unaccountably! All work must be carried out in a well ventilated fume hood behind safety shields. The ethereal diazomethane was collected directly on to KOH pellets and was stored in a −60°C Dewar until use. The reservoir of CH_2N_2 was tapped with 0.5 mm i.d. Teflon cannula tubing (Rainin Corp.) and was pumped with a Haake Buchler peristaltic pump (Model 426-2000) equipped with a 20-cm section of 1.6 mm i.d. Viton tubing (Cole–Parmer). A second piece of Teflon tubing delivers the CH_2N_2 solution to the vented reaction vessel through a punctured rubber septum. This set-up allowed for the steady and reproducible delivery of CH_2N_2 solutions to the reaction vessel.

Most of the starting halides were prepared according to the literature: $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$, X = Cl, Br, I [9]; $(\eta^5\text{-}C_5H_5)Ru(CO)_2X$, Cl [9], Br [10], I [10]; $(\eta^5\text{-}C_5Me_5)Ru(CO)_2X$, Cl [11], Br [12]; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2X$, X = Br [13], I [14]. Our preparation of the previously unreported $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Cl$ follows the exact procedure for the preparation of the $\eta^5\text{-}C_5H_5$ analogue and is characterized below. $TlOCH_2CH_3$ was used as received from Strem Chem. Co. [PPN]CN was prepared from [PPN]Cl and NaCN using a procedure similar to that reported for $[PPN]NO_2$ ($[PPN] = PPh_3NPPh_3^+$) [13].

Characterization of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2Cl$

^{1}H NMR ($CDCl_3$): δ 1.75 (s, 15H, C_5Me_5). $^{13}C\{^{1}H\}(CDCl_3)$: δ 213.9 (CO); δ 96.5 (C_5Me_5); δ 9.5 (C_5Me_5). Anal. Found: C, 51.24; H, 5.35. $C_{12}H_{15}O_2ClFe$ calc.: C, 51.01; H, 5.35%.

Synthesis of $(\eta^5\text{-}C_5R_5)M(CO)_2\text{–}CH_2X$ *complexes* (X = Cl, Br)

The reactions of the iron and ruthenium halomethyl complexes are typified by the synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2Cl$. $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ (0.240 g, 1.10 mmol) in 80 mL of Et_2O containing 6.0 g of copper powder was treated dropwise (approx. 20 drops min^{-1}) with diazomethane solution for 20 min with vigorous magnetic stirring. The initial red solution changed to bright yellow and the ν(CO) (in ether) shifted from 2040vs, 1992vs cm^{-1} to 2018vs, 1960vs cm^{-1} during this time. The solution was filtered through filter pulp into a clean Schlenk tube and the solvent removed *in vacuo*. The yellow solid was extracted with hexane, filtered through filter pulp, and concentrated. Crystallization at −40°C gave 0.240 g (94%) of yellow, crystalline (η^5-C_5H_5)Fe(CO)$_2$CH$_2$Cl [4a].

(η^5-C_5H_5)Fe(CO)$_2$CH$_2$Br: yellow crystals in 92% yield [4a]. (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$Cl: bright yellow crystals in 88% yield. Anal. Found: C, 52.99; H, 5.97. $C_{13}H_{17}O_2ClFe$ calc.: C, 52.65; H, 5.78%. m.p. 79–80°C (dec). (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$Br: yellow crystals in 94% yield. Anal. Found: C, 45.78; H, 5.03. $C_{13}H_{17}O_2BrFe$ calc.: C, 45.55; H, 5.22%. m.p. 82–84°C (dec). (η^5-C_5H_5) Ru(CO)$_2$CH$_2$Cl: yellow crystals in 95% yield [4f]. (η^5-C_5H_5)Ru(CO)$_2$CH$_2$Br: yellow crystals in 89% yield. Anal. Found: C, 30.52; H, 2.19. $C_8H_7O_2BrRu$ calc.: C, 30.39; H, 2.23%. m.p. 40–41°C (dec). (η^5-C_5Me_5)Ru(CO)$_2$CH$_2$Cl: yellow crystals in 95% yield. Anal. Found: C, 45.39; H, 4.79/ $C_{13}H_{17}O_2ClRu$ calc.: C, 45.68; H, 5.01%. m.p. 66–67°C (dec). (η^5-C_5Me_5)Ru(CO)$_2$CH$_2$Br: yellow crystals in 91% yield. Anal. Found: C, 40.46; H, 4.12. $C_{13}H_{17}O_2BrRu$ calc.: C, 40.42; H, 4.44%. m.p. 81–82°C (dec).

Direct synthesis of iodomethyl derivatives

The procedure for the iodomethyl derivatives involved several 20 min additions of CH_2N_2, with the reaction mixture being filtered into a fresh Schlenk containing 6 g of fresh Cu powder before resuming CH_2N_2 addition. Even with these measures, significant amounts of the metal-iodide starting material remained after as many as six additions.

Synthesis of iodomethyl derivatives by halide metathesis

The preparation of the (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$Br complex was typical for these metathesis reactions. (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$Br (0.10 g, 0.29 mmol) was dissolved in 5 mL of Et_2O added to a solution of NaI (1.0 g, 6.7 mmol) in 20 mL of acetone. The mixture was stirred at 20°C for 30 min and the solvent was removed *in vacuo*. Extraction with 40 mL of pentane and filtration produced a bright yellow solution which, after concentration to 5 mL, produced crystalline product at −40°C, 0.09 g (0.23 mmol, 79%) of a thermally sensitive yellow solid; m.p. 45°C (dec).

(η^5-C_5H_5)Fe(CO)$_2$CH$_2$I: yellow oil in 88% yield. (η^5-C_5H_5)Ru(CO)$_2$CH$_2$I: orange-yellow crystals in 87% yield. Anal. Found: C, 26.55; H, 2.10. $C_8H_7O_2IRu$ calc.: C, 26.46; H, 1.94%. m.p. 43–45°C. (η^5-C_5Me_5)Ru(CO)$_2$CH$_2$I: orange-yellow microcrystals in 90% yield. Anal. Found: C, 36.50; H, 3.81. $C_{13}H_{17}O_2IRu$ calc.: C, 36.04; H, 3.96%. m.p. 88–90°C (dec).

Synthesis of alkoxymethyl derivatives

Conversion of halomethyl complexes to alkoxymethyl complexes was accomplished by either using TlOR (R = ethyl) or 0.5 *M* KOR/ROH solutions (R = methyl, isopropyl). Typical preparations for both routes are given below.

(η^5-C_5Me_5)Fe(CO)$_2$–CH$_2$OCH$_2$CH$_3$. A Schlenk tube was charged with 0.10 g (0.34 mmol) of (η^5-C_5Me_5)Fe(CO)$_2$CH$_2$Cl, 15 mL of ethanol, and 0.03 mL (0.42 mmol) of $TlOCH_2CH_3$. The reaction mixture immediately turned cloudy and was stirred magnetically for 30 min. After removal of solvent *in vacuo*, the crude product was extracted with a minimum of hexane and transferred to a SiO_2 column (1 × 10 cm) made up in hexane. Elution with 6 : 1 hexane/Et_2O produced a yellow-brown band which, after solvent removal and vacuum sublimation on to a

–80°C finger, gave 0.09 g (0.29 mmol, 87%) of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_2OCH_2CH_3$ as a yellow-brown oil. MS: *m/e* 306 (100%) $[M^+]$; 278 (94%) [M – CO]; 261 (84%) [M – OEt].

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2\text{–}CH_2OCH(CH_3)_2$. A Schlenk tube was charged with 0.12 g (0.35 mmol) of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2\text{–}CH_2Br$, and 10 mL of 0.5 M $NaOCH(CH_3)_2$ in isopropanol. The mixture was stirred magnetically for 30 min and then stripped of solvent *in vacuo*. The red-brown residue was extracted in a minimum of pentane and transferred to a SiO_2 column (1 × 10 cm). Elution with hexane produced a yellow-brown zone, which upon removal of solvent and vacuum sublimation on to a –80°C finger, gave 0.10 g (0.31 mmol, 88%) of an extremely light and temperature sensitive yellow-brown oil characterized as $(\eta^5\text{-}C_5Me_5)Fe(CO)_2\text{–}CH_2OCH(CH_3)_2$. MS: *m/e* 320 (29%) $[M^+]$; 292 (62%) [M – CO]; 261 (100%) $[M - O^iPr]$.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2OCH_3$. Prepared from $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2Br$ and 0.5*M* $NaOCH_3$ in CH_3OH in 75% yield as a yellow oil. MS: *m/e* 222 (5%) $[M^+]$; 194 (100%) [M – CO]; 191 (75%) $[M - OCH_3]$ [4a].

$(\eta^5\text{-}C_5Me_5)Fe(CO)_2\text{–}CH_2OCH_3$. Prepared from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2\text{–}CH_2Br$ and 0.5*M* $KOCH_3$ in CH_3OH in 58% yield as a yellow-brown oil. MS: *m/e* 292 (15%) $[M^+]$; 264 (93%) [M – CO]; 261 (100%) $[M - OCH_3]$.

$(\eta^5\text{-}C_5Me_5)Ru(CO)_2\text{–}CH_2OCH_3$. Prepared from $(\eta^5\text{-}C_5Me_5)Ru(CO)_2\text{–}CH_2Cl$ and 0.8*M* $KOCH_3$ in CH_3OH in 66% yield as a yellow oil. MS (^{101}Ru): *m/e* 337 (76%) $[M^+]$; 309 (75%) [M – CO]; 306 (100%) $[M - OCH_3]$.

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2CN$. A Schlenk tube was charged with 0.17 g (0.6 mmol) of $(\eta^5C_5H_5)Fe(CO)_2\text{–}CH_2Cl$, 0.77 g (1.3 mmol) of [PPN]CN, and 20 mL of CH_2Cl_2. The mixture was stirred magnetically for 30 min and then the solvent was removed *in vacuo*. The residue was slurried in 20 mL Et_2O and filtered onto a 2 × 5 cm column of Al_2O_3(III) made up in Et_2O. Elution with 2 : 1 CH_2Cl_2/Et_2O produced a yellow band. Recrystallization from 1 : 1 CH_2Cl_2/Et_2O at –40°C gave 0.12 g (0.55 mmol, 92%) of yellow crystalline $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2CH_2CN$. MS: *m/e* 217 (100%) $[M^+]$; 189 (92%) [M – CO]; 191 (11%) [M – CN]; 177 (29%) $[M - CH_2CN]$ [6a].

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