APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* **12**, 801–807 (1998)

# The Synthesis and Characterization of Metal-containing Vinylic Monomers of Iron and Tungsten

Selwyn F. Mapolie,[1]* John R. Moss[2] and Gregory S. Smith[1]
[1]Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa
[2]Department of Chemistry University of Cape Town, Private Bag Rondebosch, 7701, South Africa

**A series of metal-containing vinylic monomers of the type $L_nM(COC_6H_4CH{=}CH_2)$ and $L_nM(COCH{=}CHC_6H_5)$ [$L_nM = (\eta^5\text{-}C_5H_5)Fe(CO)_2$, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3$] were prepared by the reaction of the appropriate metal anion with either 4-vinylbenzoyl chloride or cinnamoyl chloride. $(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{-}COCH{=}CH_2$ was prepared by the reaction of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and acryloyl chloride, whereas the compound $(\eta^5\text{-}C_5H_5)(CO)_2\text{-}Fe(C_6H_4CH{=}CH_2)$ was prepared via a transmetallation reaction using a palladium catalyst. All compounds were fully characterized using FTIR, $^1H$ and $^{13}C$ NMR spectroscopy and mass spectrometry. © 1998 John Wiley & Sons, Ltd.**

**Keywords: metal-containing vinylic monomers; vinylbenzoyl complexes; cinnamoyl complexes; tungsten–olefin monomers; iron–olefin monomers**

*Received 1 December 1997; accepted 26 February 1998*

## 1 INTRODUCTION

Metal-containing vinylic monomers are organometallic compounds in which a metal centre is bonded to an organic moiety containing a vinylic functional group. Such compounds have previously been used in the preparation of organometallic polymers.[1–3]

A number of these vinyl species have been synthesized previously,[4,5] but in most cases the metal centre is bound to the organic moiety via an M–C $\pi$-bond, as in vinylferrocene.[6]

Although there are some examples[7–10] in which the vinyl-containing organic moiety is bonded to the metal centre via a M–C $\sigma$-bond, many of these compounds have not been well characterized. Thus King and Bisnette, for example, prepared the compound $Cp(CO)_2Fe(COCH{=}CHC_6H_5)$,[8] and Nesmeyanov prepared $Cp(CO)_3W(COCH{=}CHC_6H_5)$;[9] however, in both cases, the complexes were only partially characterized.

In this paper, we now report the synthesis of a number of new vinylic metal-containing compounds, **1–3** and **7**.

The new compounds have been fully characterized by FTIR, $^1H$ and $^{13}C$ NMR spectroscopy, microanalysis and mass spectrometry. In addition to the new compounds we also report improved yields and more complete characterization data for the known compounds **4–6**.

## 2 EXPERIMENTAL

### 2.1 Apparatus and materials

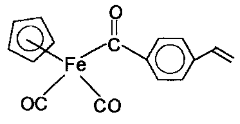
All reactions were carried out under nitrogen using standard Schlenk tube techniques. Tetrahydrofuran (THF) and toluene were dried over sodium/benzophenone and distilled under nitrogen before use. $[CpFe(CO)_2]_2$, 4-bromo-1-butene, acryloyl chloride, *trans*-cinnamoyl chloride, 4-vinylbenzoic acid, 4-bromostyrene and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich, and were used without further purification. 4-Vinylbenzoic acid was converted to the acid chloride using neat $SOCl_2$ in the standard manner.[11] $[Cp^*Fe(CO)_2]_2$ was obtained from Strem Chemicals, and $[CpW(CO)_3]_2$ was prepared according to a literature procedure.[12] All column chromatography was done on either deactivated alumina 90 (70–230 mesh) or silica gel (70–230 mesh), obtained from Merck. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 PC FTIR spectrophotometer, using solution cells with NaCl windows unless

---

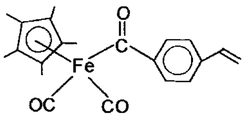
* Correspondence to: Selwyn F. Mapolie, Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa.

Contract/grant sponsor: Foundation for Research Development (FRD) of South Africa; Contract/grant sponsor: Research Committees of The University of the Western Cape.

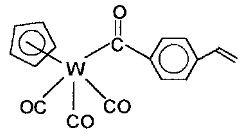
CCC 0268–2605/98/120801–07 $17.50



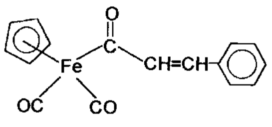
**1**



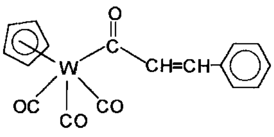
**2**



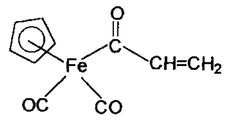
**3**



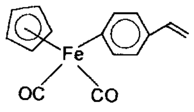
**4**



**5**



**6**



**7**

stated otherwise. $^{1}$H and $^{13}$C NMR spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained with a V. G. Micromass 16F spectrometer, operating at 70 eV ionizing voltage. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Melting points were determined on a Fisher–Johns hot-stage melting-point apparatus, and are uncorrected.

## 2.2 Preparation of $Cp(CO)_2Fe(COC_6H_4CH{=}CH_2)$ (1)

A solution of $[CpFe(CO)_2]_2$ (1.00 g, 2.84 mmol) in THF (20 ml) was stirred over a sodium amalgam (0.30 g Na; 4.0 ml Hg) for 2 h at room temperature. The resulting solution was added dropwise with stirring to a cooled solution of 4-vinylbenzoyl chloride (0.95 g, 5.67 mmol) in THF (5.0 ml) at −78°C. After the addition was complete, the solution was gradually allowed to warm to room temperature. The dark red–brown solution was stirred at room temperature for three days. The solvent was removed under reduced pressure and the residue extracted with $CH_2Cl_2$ (3 × 30 ml). The extracts were filtered and the solvent removed by rotary evaporation. The residue was dissolved in a minimum amount of benzene, and chromatographed on a silica gel column (6 cm × 2.5 cm), using benzene as eluent. This resulted in four bands. The first band gave a yellow oil on removal of the solvent and appears to be some unidentified organic by-product (containing no terminal carbonyls). The second band gave a red solid which was identified as the dimer, $[CpFe(CO)_2]_2$. The third band was found to contain the product, $Cp(CO)_2Fe(COC_6H_4CH{=}CH_2)$ (**1**). This gave bright yellow crystals (0.92 g, 53%), after recrystallization from a $CH_2Cl_2$ solution to which hexane was added. The fourth fraction was isolated as an orange solid and confirmed to be the by-product, $[CpFe(CO)_2Cl]$, by TLC comparison with an authentic sample, and comparing its IR spectrum with that reported in the literature.[13,14]

## 2.3 Preparation of $Cp^*(CO)_2Fe(COC_6H_4CH{=}CH_2)$ (2)

A solution of $Na[Cp^*Fe(CO)_2]$ (2.02 mmol) was prepared by stirring $[Cp^*Fe(CO)_2]_2$ (0.50 g, 1.01 mmol) in THF (20 ml) over a sodium amalgam (0.30 g Na; 4.0 ml Hg) for 18 h at room temperature. This mixture was added to a solution of 4-vinylbenzoyl chloride (0.34 g, 2.02 mmol) in THF (5 ml) at −78°C. After the addition was complete, the solution was allowed to warm to room temperature. The orange–brown mixture was stirred for 20 h at this temperature. The solvent was removed by rotary evaporation, and the residue extracted with $CH_2Cl_2$ (3 × 30 ml). Filtration of the extracts and removal of the solvent yielded an orange oil. The oil was chromatographed on a silica gel column (6 cm × 2.5 cm). Elution with benzene resulted in three fractions, namely a dark-red band moving closest to the solvent front, a yellow band following behind this band, and an orange–red band which moved very slowly. The first band was confirmed to be the starting material, [Cp*Fe-$(CO)_2]_2$. The second band was found to be the product, Cp*$(CO)_2$Fe($COC_6H_4CH$=$CH_2$) (**2**). This was isolated as a yellow oil and was recrystallized from hexane at −78°C to produce the pure product (0.29 g, 38%). The third band was the compound [Cp*Fe$(CO)_2$Cl].[15,16]

## 2.4 Preparation of (Cp$(CO)_3$W($COC_6H_4CH$=$CH_2$)) (3)

Cyclopentadienyltungsten tricarbonyl dimer, $[CpW(CO)_3]_2$ (0.702g, 1.05 mmol) was dissolved in THF (20 ml) and the solution stirred over a sodium amalgam (0.30 g Na; 4.0 ml Hg) at room temperature for 2 h. Using a syringe, the resulting green–grey solution was added dropwise to a solution of 4-vinylbenzoyl chloride (0.35 g, 2.10 mmol) in THF (5 ml) at −78°C. The reaction mixture was allowed to warm to room temperature, and the orange solution was stirred overnight. Removal of the solvent left an oily orange residue. This was extracted with $CH_2Cl_2$ (3 × 30 ml), filtered and the solvent removed from the filtrate using a rotary evaporator to give an orange oil. The oil was chromatographed on a silica gel column (6 cm × 2.5 cm) using benzene as eluent. Two components were observed, but extensive decomposition occurred on the column. The first band was eluted as a dark-orange fraction which decomposed rapidly in solution and in the solid state. The second fraction gave a lighter-orange band, which was found to be the product, Cp$(CO)_3$W-($COC_6H_4CH$=$CH_2$) (**3**). Removal of the solvent, and recrystallization of the remaining orange oil from hexane at −78°C, gave the product as an orange solid (0.27 g, 30%).

## 2.5 Preparation of Cp$(CO)_2$Fe(COCH=$CH_2$) (6)

A solution of Na[CpFe$(CO)_2$] (5.65 mmol) was prepared by stirring $[CpFe(CO)_2]_2$ (1.00 g, 2.82 mmol) over a sodium amalgam (0.30 g Na; 4.0 ml Hg) in THF (20 ml) for 2 h. This solution was added dropwise to a solution of acryloyl chloride (0.46 ml, 5.65 mmol) in THF (5.0 ml) which had been cooled to −78°C. The resulting dark-green reaction mixture was stirred for 30 min at −78°C; on warming gradually to room temperature, it turned yellow–orange and stirring was continued for a further 18 h at room temperature. The solvent was removed using a rotary evaporator, and the dark-orange residue extracted with $CH_2Cl_2$ (3 × 30 ml) and filtered by gravity. The filtrate was evaporated on a rotary evaporator. The resulting oil was taken up in a small volume of benzene, and the solution chromatographed on a silica gel column (6 cm × 2.5 cm), using benzene as eluent. An orange–yellow band was collected and removal of the solvent yielded an orange oil. The orange oil was purified by low-temperature (−78°C) recrystallization from hexane: thus when a concentrated hexane solution of the oil was cooled to −78°C a yellow solid was precipitated. The mother liquor was syringed off and the yellow solid washed with ice-cold hexane (2 × 5 ml). On warming the solid to room temperature, an orange oil was obtained which was identified as Cp$(CO)_2$Fe(COCH=$CH_2$) (**6**) (0.80 g, 61%.)

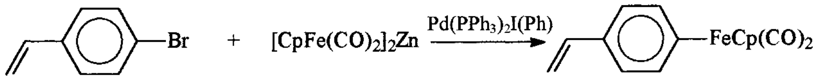
## 2.6 Preparation of Cp$(CO)_2$Fe($C_6H_4CH$=$CH_2$) (7)

A solution of $[CpFe(CO)_2]_2$ (0.50 g, 1.41 mmol) in THF (12 ml) was stirred over a sodium amalgam (0.30 g Na; 4.0 ml Hg) for 1.5 h at room temperature. This solution was added to a solution of dry $ZnCl_2$ (0.20 g 1.41 mmol) in THF (5.0 ml), yielding a green mixture. 4-Bromostyrene (0.40 ml, 2.82 mmol) was syringed into the reaction mixture; thereafter the catalyst $Pd(PPh_3)_2I(Ph)$ (0.072 g, 0.0864 mmol) was added. A darkening of the reaction mixture was observed. The reaction was allowed to proceed for two days at room temperature. The solvent was removed by rotary evaporation, and the residue extracted with hexane and filtered. The solvent was removed by rotary evaporation, leaving an orange–yellow oil which was chromatographed on an alumina column (5 cm × 2.5 cm), using hexane as eluent. Two yellow fractions were collected after elution. The first band was isolated as a yellow oil, which was found to be the compound Cp$(CO)_2$Fe$C_6H_4$CH-(Br)$CH_3$. The compound Cp$(CO)_2$Fe-($C_6H_4CH$=$CH_2$) (**7**) was found in the second band, and isolated as an orange–yellow oil. Purification of the product by low-temperature (−78°C) recrystallization in hexane, gave an oil (0.10 g, 12%).

# 3 RESULTS AND DISCUSSION

## 3.1 Synthesis of the monomers

The metal-containing vinylic compounds **1–6** were



[2]

prepared by the reaction of the metal carbonyl anion with the appropriate acid chloride, as depicted in Eqn [1].

$$Na[CpM(CO)_n] + RCOCl \rightarrow Cp(CO)_nM(COR) + NaCl \qquad [1]$$

**1:** $M = Fe,\ n = 2,\ Cp = \eta^5 - C_5H_5,\ R = -C_6H_4CH = CH_2$

**2:** $M = Fe,\ n = 2,\ Cp = \eta^5 - C_5Me_5(= Cp^*),\ R = -C_6H_4CH = CH_2$

**3:** $M = W,\ n = 3,\ Cp = \eta^5 - C_5H_5,\ R = -C_6H_4CH = CH_2$

**4:** $M = Fe,\ n = 2,\ Cp = \eta^5 - C_5H_5,\ R = -CH = CHC_6H_5$

**5:** $M = W,\ n = 3,\ Cp = \eta^5 - C_5H_5,\ R = -CH = CHC_6H_5$

**6:** $M = Fe,\ n = 2,\ Cp = \eta^5 - C_5H_5,\ R = -CH = CH_2$

All of these compounds, except **6**, were isolated as yellow or orange–yellow solids which were stable in air at room temperature in the solid state. Compound **6** was isolated as a yellow–brown oil which appeared to be thermally unstable at room temperature but could be stored for several weeks at −20°C without appreciable decomposition. Solutions of all the compounds decompose quite rapidly over a couple of hours in the absence of an inert atmosphere. In some cases the yields of the compounds are not very high, but generally they range between 30 and 70% with the lowest yield being obtained for compound **3**. These yields, together with elemental analysis and melting points, are given in Table 1. Compounds **1–3** are new, whereas compounds **4–6** were prepared essentially by the literature methods, with slight modifications.[8,9] Compounds **4–6** had previously not been fully characterized and we now report complete characterization data for these species. We have also managed to prepare **6** in an improved yield of 61%, compared with the 5% reported by King and Bisnette.[8]

**Table 1** Yields, melting points and analytical data for compounds **1–7**

| Compound | Yield (%)[a] | M.p. (°C) | Analysis[b] C | H |
|---|---|---|---|---|
| 1 | 53 | 46–47 | 62.33 (62.36) | 3.94 (3.93) |
| 2 | 38 | 66–68 | 66.80 (66.67) | 5.91 (5.87) |
| 3 | 30 | 75 (dec.) | 44.26 (43.99) | 2.74 (2.61) |
| 4 | 70 | 91–92 | 62.22 (62.36) | 3.83 (3.93) |
| 5 | 47 | 101–104 | 44.37 (43.99) | 2.58 (2.61) |
| 6 | 61 | Oil | —[c] | —[c] |
| 7 | 12 | Oil | —[c] | —[c] |

[a] Based on the anion used.
[b] Calculated values in parentheses.
[c] Due to the instability of the compounds, satisfactory microanalyses were not obtained.

Attempts to decarbonylate the acyl species **1–6** to form the corresponding metal–aryl complexes were not successful. In this regard both thermal and chemical decarbonylation using Wilkinson's complex, $RhCl(PPh_3)_3$, were attempted.

The aryl compound **7** thus had to be prepared by a different synthetic route. The one that proved to be successful involved the transmetallation reaction of 4-bromostyrene with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Zn$ as outlined in Eqn [2].

This synthetic route is based on the procedure developed by Artamkina *et al.*, who reported the synthesis of a series of transition metal–aryls starting from aryl halides.[17,18]

The low yield obtained for compound **7** can possibly be ascribed to the use of an aryl bromide instead of the more reactive aryl iodide, which was not available to us. Fauvarque and co-workers reported that the use of aryl bromides can be up to $10^4$ times less reactive than the corresponding iodides.[19] Compound **7** was isolated as a yellow oil, which is only stable at temperatures of around −20°C. Decomposition of the compound is observed in the presence of air and if the compound is kept at room temperature for long periods.

Characterization data for **7**, together with those for all the other compounds prepared, are given in Tables 1 and 2 and are discussed below.

## 3.2 IR spectra

The IR spectra of the previously prepared com-

**Table 2** Infrared data for compounds **1–7**

| Compound | $\nu$(CO)(cm$^{-1}$)$^a$ | | | | |
|---|---|---|---|---|---|
| **1** | 2022 (s) | 1962 (s) | 1608 (m) | 1587 (m) | |
| **2** | 2000 (s) | 1940 (s) | 1604 (w) | 1578 (m) | |
| **3** | 2019 (m) | 1923 (s, br), | 1606 (w) | 1582 (w) | |
| **4** | 2022 (s) | 1962 (s) | 1634 (w) | 1584 (w) | |
| **5** | 2018 (m) | 1918 (s, br) | 1628 (w) | 1579 (w) | 1568 (w) |
| **6** | 2023 (s) | 1960 (s) | 1636 (m) | 1600 (m) | 1582 (w) |
| **7** | 2013 (s) | 1955 (s) | | | |

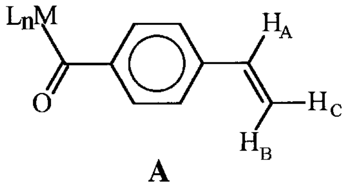
[a] Recorded in $CH_2Cl_2$, using solution cells with NaCl windows; s = strong, m = medium, br = broad, w = weak.

pounds, viz. **4–6**, are in good agreement with those reported in the literature.[8,9]

The new vinylbenzoyl derivatives **1–3** have spectral characteristics which are similar to those of analogous systems. Thus the iron–vinylbenzoyl compound **1** shows two strong $\nu$(CO) bands at 2022 and 1962 cm$^{-1}$ for the terminal carbonyls. These bands are at positions similar to those found for simple systems of the type $Cp(CO)_2Fe(COR)$. The analogous pentamethylcyclopentadienyl (Cp*) derivative **2** shows $\nu$(CO) bands at lower frequencies than the unsubstituted cyclopentadienyl derivative. Compound **2** thus has strong bands at 2000 cm$^{-1}$ and 1940 cm$^{-1}$. The significant lowering of the (CO) frequency in going from **1** to **2** is due to the strong electron-donating effect of the methyl groups on the cyclopentadienyl ring. This in turn leads to an increase in the electron density on the metal, which results in the lowering of the CO stretching frequencies for compound **2**. The tungsten derivative **3** shows a sharp band of medium intensity at 2019 cm$^{-1}$ together with a strong broad band at 1923 cm$^{-1}$. These frequencies are similar to those obtained for compounds of the type $Cp(CO)_3WCOR$. The iron–aryl compound **7** exhibits strong $\nu$(CO) bands at 2013 and 1955 cm$^{-1}$, similarly to other iron–aryl complexes reported in the literature.[18]

## 3.3 NMR spectra

The $^1$H NMR spectra for the known compounds **4–6** compare favourably with the data previously reported in the literature.[8,9] The novel compounds **1–3** and **7** exhibit similar resonances which are characteristic of vinylbenzoyl derivatives. Hence the $^1$H spectrum shows a well-resolved AMX splitting pattern for the vinylic protons which is similar to that observed in the spectra for compounds such as vinylferrocene.[20] The chemical-shift assignments for **1–3** are based on structure **A** and are listed in Table 3.



**A**

For all the compounds, protons $H_A$, $H_B$ and $H_C$ are magnetically non-equivalent, resulting in coupling between $H_A$ on the one hand and protons $H_B$ and $H_C$ on the other. Geminal coupling ($H_B$–$H_C$) is not observed in any of the complexes. The *trans* ($J_{AB}$) and *cis* ($J_{AC}$) coupling constants are around 17.5 and 11 Hz respectively. Typically a doublet is observed for proton $H_C$, a doublet for $H_B$, and a doublet of doublets for $H_A$ in the spectra of these vinyl derivatives. Changing the metal centre from iron to tungsten has no significant effect on the chemical shifts of the vinylic protons.

The rest of the $^1$H NMR spectra are as expected with the Cp ligand in compounds **1** and **3** giving a sharp singlet at $\delta = 4.93$ ppm and $\delta = 5.70$ ppm respectively. The pentamethylcyclopentadienyl compound **2** shows a sharp singlet at $= 1.80$ ppm for the methyl substituents on the Cp ring. A typical splitting pattern for a *para*-substituted aromatic ring is observed in the expected region of the spectra for all the compounds except **2**, which shows a sharp singlet in this region.

The $^{13}$C NMR spectral data for compounds **4–7** are also given in Table 3. Assignments were made by using a DEPT (distortionless enhancement of polarization transfer) pulse experiment.

## 3.4 Mass spectra

The mass spectra of the vinylic derivatives show similar characteristics (Tables 4 and 5). Firstly, in none of the spectra is any parent ion observed, and secondly, most of the compounds show at least two

**Table 3** $^1H$ and $^{13}C$ NMR spectral data

| Compound | $^1H$ NMR<br>$\delta$ (ppm)[a] | Assignment | $^{13}C$ NMR<br>$\delta$ (ppm)[a] | Assignment |
|---|---|---|---|---|
| **1** | 4.93 (s, 5H) | $C_5\mathit{H}_5$ | 86.24 | $\mathit{C}_5H_5$ |
| | 5.32 (d, 1H, $J_{cis}$ = 10.9 Hz) | $FeCOC_6H_4CH{=}C\mathit{H}_2$ | 115.51 | $FeCOC_6H_4CH{=}\mathit{C}H_2$ |
| | 5.81 (d, 1H, $J_{trans}$ = 17.6 Hz) | $FeCOC_6H_4CH{=}C\mathit{H}_2$ | 125.82, 126.47, 139.34, 149.40 | $FeCO\mathit{C}_6H_4CH{=}CH_2$ |
| | 6.72 (dd, 1H, $J$ = 17.6, 10.9 Hz) | $FeCOC_6H_4C\mathit{H}{=}CH_2$ | 136.04 | $FeCOC_6H_4\mathit{C}H{=}CH_2$ |
| | 7.40 (d, 2H, $J$ = 8.5 Hz) | $FeCOC_6\mathit{H}_4CH{=}CH_2$ | 213.94 | $\mathit{C}O$ (terminal) |
| | 7.45 (d, 2H, $J$ = 8.5 Hz) | $FeC_6\mathit{H}_4CH{=}CH_2$ | | |
| **2** | 1.80 (s, 15H) | $C_5(C\mathit{H}_3)_5$ | 9.66 | $C_5(\mathit{C}H_3)_5$ |
| | 5.30 (d, 1H, $J_{cis}$ = 10.8 Hz) | $FeCOC_6H_4CH{=}C\mathit{H}_2$ | 97.23 | $\mathit{C}_5(CH_3)_5$ |
| | 5.79 (d, 1H, $J_{trans}$ = 17.6 Hz) | $FeCOC_6H_4CH{=}C\mathit{H}_2$ | 115.03 | $FeCOC_6H_4CH{=}\mathit{C}H_2$ |
| | 6.72 (dd, 1H, $J$ = 17.6, 10.9 Hz) | $FeCOC_6H_4C\mathit{H}{=}CH_2$ | 125.75, 126.63, 138.95, 148.32 | $FeCO\mathit{C}_6H_4CH{=}CH_2$ |
| | 7.42 (s, 4H) | $FeCOC_6\mathit{H}_4CH{=}CH_2$ | 136.29 | $FeCOC_6H_4\mathit{C}H{=}CH_2$ |
| | | | 216.14 | $\mathit{C}O$ (terminal) |
| **3** | 5.34 (d, 1H, $J_{cis}$ = 10.9 Hz) | $WCOC_6H_4CH{=}C\mathit{H}_2$ | 96.17 | $\mathit{C}_5H_5$ |
| | 5.70 (s, 5H) | $C_5\mathit{H}_5$ | 115.98 | $WCOC_6H_4CH{=}\mathit{C}H_2$ |
| | 5.82 (d, 1H, $J_{trans}$ = 17.6 Hz) | $WCOC_6H_4CH{=}C\mathit{H}_2$ | 126.02, 128.59, 140.64, 148.76 | $WCO\mathit{C}_6H_4CH{=}CH_2$ |
| | 6.71 (dd, 1H, $J$ = 17.6, 10.9 Hz) | $WCOC_6H_4C\mathit{H}{=}CH_2$ | 136.15 | $WCOC_6H_4\mathit{C}H{=}CH_2$ |
| | 7.39 (d, 2H, $J$ = 8.5 Hz) | $WCOC_6\mathit{H}_4CH{=}CH_2$ | 219.95 | $\mathit{C}O$ (terminal) |
| | 7.49 (d, 2H, $J$ = 8.5 Hz) | $WCOC_6\mathit{H}_4CH{=}CH_2$ | | |
| **4** | 4.85 (s, 5H) | $C_5\mathit{H}_5$ | 86.42 | $\mathit{C}_5H_5$ |
| | 6.60 (d, 1H, $J$ = 15.7 Hz) | $FeCOC\mathit{H}{=}CHC_6H_5$ | 128.22, 128.74, 135.07 | $FeCOCH{=}CH\mathit{C}_6H_5$ |
| | 6.93 (d, 1H, $J$ = 15.7 Hz) | $FeCOCH{=}C\mathit{H}C_6H_5$ | 129.51 | $FeCO\mathit{C}H{=}CHC_6H_5$ |
| | 7.20–7.56 (m, 5H) | $FeCOCH{=}CHC_6\mathit{H}_5$ | 138.58 | $FeCOCH{=}\mathit{C}HC_6H_5$ |
| | | | 213.98 | $\mathit{C}O$ (terminal) |
| **5** | 5.65 (s, 5H) | $C_5\mathit{H}_5$ | 95.83 | $\mathit{C}_5H_5$ |
| | 6.79 (d, 1H, $J$ = 15.7 Hz) | $WCOC\mathit{H}{=}CHC_6H_5$ | 128.47, 128.74, 134.11 | $WCOCH{=}CH\mathit{C}_6H_5$ |
| | 6.98 (d, 1H, $J$ = 15.7 Hz) | $WCOCH{=}C\mathit{H}C_6H_5$ | 129.68 | $WCO\mathit{C}H{=}CHC_6H_5$ |
| | 7.40–7.64 (m, 5H) | | 142.74 | $WCOCH{=}\mathit{C}HC_6H_5$ |
| | | | 219.95 | $\mathit{C}O$ (terminal) |
| **6** | 4.91 (s, 5H) | $C_5\mathit{H}_5$ | 86.42 | $\mathit{C}_5H_5$ |
| | 5.30 (d, 1H) | $FeCOCH{=}C\mathit{H}_2$ | 115.70 | $FeCOCH{=}\mathit{C}H_2$ |
| | 5.39 (d, 1H) | $FeCOCH{=}C\mathit{H}_2$ | 148.56 | $FeCO\mathit{C}H{=}CH_2$ |
| | 6.55 (dd, 1H) | $FeCOC\mathit{H}{=}CH_2$ | 214.10 | $\mathit{C}O$ (terminal) |
| **7** | 4.84 (s, 5H) | $C_5H_5$ | —[b] | |
| | 5.10 (d, 1H, $J_{CA,cis}$ = 10.9 Hz) | $FeC_6H_4CH{=}C\mathit{H}_2$ | | |
| | 5.60 (d, 1H, $J_{BA,trans}$ = 17.7 Hz) | $FeC_6H_4CH{=}C\mathit{H}_2$ | | |
| | 6.58 (dd, 1H, $J$ = 17.6, 10.9 Hz) | $FeC_6H_4C\mathit{H}{=}CH_2$ | | |
| | 7.00–7.39 (m, 4H) | $FeC_6\mathit{H}_4CH{=}CH_2$ | | |

[a] $CDCl_3$ as solvent.
[b] Spectrum not recorded due to instability of compound.

fragmentation pathways. The first fragmentation pathway involves the initial loss of all the carbonyl groups from the molecular ion, followed by loss of the organic fragments. It is assumed that initially we have decarbonylation of the acyl species followed by sequential loss of the terminal carbonyl groups. This is similar to the process in analogous acyl species of the types $CpFe(CO)_2(COR)$ and $CpW(CO)_3(COR)$.[21–23]

The second fragmentation pathway involves the initial loss of the organic group. In the case of the iron compounds this leads to the formation of the ion $[CpFe(CO)_3{}^+]$, which is a characteristic fragment in the mass spectra of acyl derivatives of the type $Cp(CO)_2Fe(COR)$. The resulting ion undergoes further decomposition by the sequential loss of the carbonyl groups, followed by the cyclopentadienyl group, to yield the species $Fe^+$ ($m/z = 56$).

The pentamethylcyclopentadienyl iron derivative **2** shows only the first fragmentation pathway, i.e. the one commencing with the loss of carbonyl groups. The tungsten compounds, however, show fragmentation pathway similar to those of the iron analogues.

**Table 4** Mass spectral data for the compounds $L_nM(COC_6H_4CH{=}CH_2)$, where $L_nM = [(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3]$ (**1–3**)

| | Relative peak intensity | | |
|---|---|---|---|
| Ion[a] | **1**[b] | **2**[c] | **3**[d] |
| P | — | — | — |
| P-CO | — | 28 | 62 |
| P-2CO | 100 | 12 | 34 |
| P-3CO | — | 100 | 92 |
| P-$C_6H_4CH{=}CH_2$ | 0.8 | — | 37 |
| P-CO-$C_6H_4CH{=}CH_2$ | 3 | — | 3 |
| P-2CO-$C_6H_4CH{=}CH_2$ | — | — | 5 |
| P-3CO-$C_6H_4CH{=}CH_2$ | 53 | 12 | — |
| P-4CO-$C_6H_4CH{=}CH_2$ | — | — | 14 |
| $CH_2{=}CHC_6H_4CO$ | 51 | 2 | 100 |
| $CH_2CHC_6H_4$— | 25 | 2 | — |
| M[e] | 64 | 9 | — |
| $C_6H_5$— | — | — | 23 |
| CO/$C_2H_4$ | — | 40 | — |

[a] P = molecular ion. All ions have a single positive charge; these are suggested assignments.
[b] Peak intensities relative to base peak *m/z* 252.
[c] Relative to base peak *m/z* 294.
[d] Relative to base peak *m/z* 131.
[e] M = 'naked metal'.

**Table 5** Mass spectral data for $C_5H_5(CO)_3W(COCH{=}CHC_6H_5)$ (**5**)

| Ion[a] | *m/z* | Relative peak intensity **5**[b] |
|---|---|---|
| P | 464 | — |
| P-CO | 436 | 24 |
| P-2CO | 408 | 14 |
| P-3CO | 380 | 43 |
| P-4CO | 352 | 23 |
| P-CO-$C_6H_5$—$C_2H_2$ | 338 | 04 |
| P-4CO-CH | 339 | 07 |
| P-2CO-$C_6H_5$—$C_2H_2$ | 317 | 06 |
| P-4CO-$C_6H_5$-$C_2H_2$ | 261 | 17 |
| $C_6H_5CH{=}CHCO$ | 131 | 100 |
| $C_6H_5$— | 72 | 23 |
| CO/$C_2H_4$ | 28 | 87 |

[a] P = molecular ion. All ions have a single positive charge; these are suggested assignments.
[b] Relative to base peak *m/z* 131.

## 4 CONCLUSION

Some metal-containing vinylic monomers of iron and tungsten have been successfully prepared, either by the reaction of the metal anion with the appropriate acyl halide, or using a palladium-catalysed cross-coupling reaction. All the new compounds have been fully characterized by conventional techniques. We are currently in the process of evaluating these metal-containing vinylic compounds as potential monomers in the preparation of organometallic polymers and will report on our results in a later publication.

*Acknowledgments* We gratefully acknowledge the financial support of the Foundation for Research Development (FRD) of South Africa and the Research Committees of The University of the Western Cape and the University of Cape Town.

## REFERENCES

1. C. U. Pittman Jr, C. E. Carraher Jr, J. E. Sheets, M. D. Timken and M. Zeldin, *Inorganic and Metal-Containing Polymeric Materials,* Plenum Press, New York, 1990, p. 1.
2. I. Manners, *Angew. Chem., Int. Ed. Engl.* **35**, 1602 (1996).
3. M. Bochmann, J. Lu and R. D. Cannon, *J. Organometal. Chem.* **518**, 97 (1996).
4. D. W. Macomber, W. P. Hart and M. D. Rausch, *J. Am. Chem. Soc.* **104**, 884 (1982).
5. D. W. Macomber, W. Spink and M. D. Rausch, *J Organometal. Chem.,* **250**, 311 (1983).
6. C. U. Pittman Jr, *Organometallic Polymers,* Academic Press, New York, 1978, p. 1.
7. S. Kher and T. Nile, *Transition Metal Chem.* **16**, 28 (1991).
8. R. B. King and M. B. Bisnette, *J. Organometal. Chem.* **2**, 15 (1964).
9. A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR., Ser. Khim.* **10**, 2375 (1978).
10. S. Achar, R. J. Puddephatt and J. D. Scott, *Can. J. Chem.,* **74**, 1983 (1996).
11. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tachell, *Vogel's Textbook of Practical Organic Chemistry,* 5th edn, Longmans, UK; 1989, p.705.
12. A. R. Manning, P. Hackett, R. Birdwhistell and P. Soye, *Inorg. Synth.* **28**, 148 (1990).
13. B. D. Dombek and R. J. Angelici, *Inorg. Chim. Acta* **7**(2), 345 (1973).
14. O. A. Gansow, D. A. Schoxnayder and B. Y. Kimura, *J. Am.. Chem. Soc.* **94**(10), 3406 (1972).
15. P. Jutzi and A. Mix, *Chem. Ber.* **123**, 1043 (1990).
16. W. Clegg, N. A. Compton, R. J. Errington and N. C. Norman, *J. Chem. Soc., Dalton Trans.* 1671 (1988).
17. G. A. Artamkina, A. Y. Mil'chenko, N. A. Bumagin, I. P. Beletskaya and O. A. Reutov, *Izv. Akad. Nauk. SSSR., Ser. Khim.* **3**, 700 (1987).
18. G. A. Artamkina, A. Y. Mil'chenko, N. A. Bumagin, I. P. Beletskaya and O. A. Reutov, *Metalloorgan. Khim.* **1**, 34 (1988).
19. J. F. Fauvarque, F. Pfluger and M. Troupel, *J. Organometal. Chem.* **208**, 419 (1981).
20. M. D. Rausch and A. Siegel, *J. Organometal. Chem.* **11**, 317 (1968).
21. R. B. King, *J. Am. Chem. Soc.* **90**, 1417 (1968).
22. R. E. Winters and R. W. Kiser, *J. Organometal. Chem.* **4**, 190 (1965).
23. E. Schumacher and R. Taubenest, *Helv. Chim. Acta* **49**, 1447 (1966).