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THE SYNTHESIS AND ^{1}H NMR STUDY OF VINYL ORGANOMETALLIC MONOMERS: (η^5-$C_5H_4CH{=}CH_2$)M(CO)$_2$(NO) (M = Cr, Mo, W) AND (η^5-$C_5H_4CH{=}CH_2$)M(CO)$_2$ (M = Co, Rh, Ir)

DAVID W. MACOMBER, W. CRAIG SPINK, and MARVIN D. RAUSCH*
Department of Chemistry, University of Massachusetts, Amherst, MA 01003 (U.S.A.)

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Summary

A reaction between 6-methylfulvene and lithium diisopropylamide in THF solution produces vinylcyclopentadienyllithium in yields of 85–95%. The ^{1}H NMR spectrum of this air-sensitive organolithium reagent has been recorded in THF-d_8. Reactions of vinylcyclopentadienyllithium with Group VIB metal hexacarbonyls followed by treatment with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide afford the new vinyl organometallic monomers (η^5-$C_5H_4CH{=}CH_2$)M(CO)$_2$(NO) (M = Mo, W). Vinylcyclopentadienyllithium also serves as a convenient precursor to a series of (η^5-vinylcyclopentadienyl)dicarbonylmetal monomers of cobalt, rhodium, and iridium. The ^{1}H NMR spectra of these vinylcyclopentadienylmetal derivatives have been compared as a function of the metal.

Introduction

In our continuing study of the synthesis of functionally substituted cyclopentadienylmetal compounds [1–3], we have prepared several new organometallic monomers. During the course of this investigation the ^{1}H NMR spectra of these vinyl derivatives have been recorded and compared as a function of the metal.

Results and discussion

Recently we have developed a convenient method for the synthesis of vinylcyclopentadienylmetal compounds [2]. Treatment of 6-methylfulvene with lithium diisopropylamide in THF solution gave vinylcyclopentadienyllithium (I) in yields of 85–95%. Compound I is an air-sensitive white solid with properties similar to cyclopentadienyllithium. The ^{1}H NMR spectrum of I was recorded in THF-d_8. A pair of apparent triplets (A_2B_2 pattern) was observed for the cyclopentadienyl protons. This A_2B_2 pattern is typical for mono-substituted cyclopentadienylmetal

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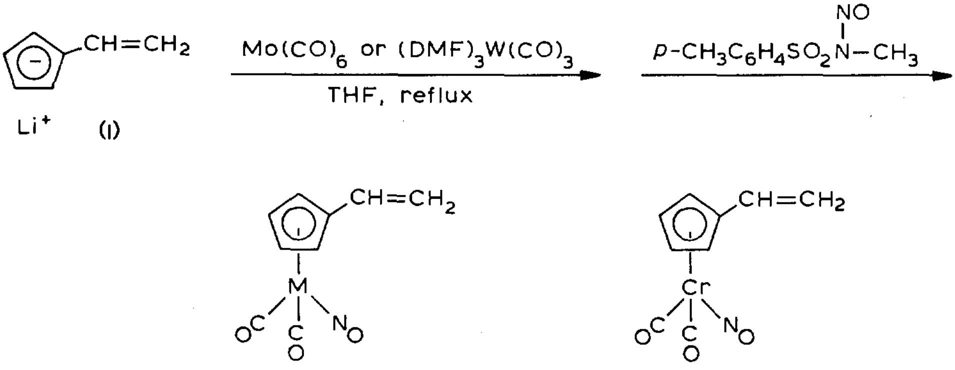
(I)

compounds [4]. Compound I also exhibits a well-resolved ABX pattern for the vinylic protons; styrene [5] and vinylferrocene [6] exhibit a similar pattern. The *trans, cis,* and *geminal* coupling constants associated with the vinylic protons of I are 17, 11, and 3 Hz, respectively.

Organolithium reagent I reacted with molybdenum hexacarbonyl and with tris(dimethylformamide)tricarbonyltungsten in refluxing THF to give η^5-vinylcyclopentadienyl derivatives of these metals. Nitrosylation of the intermediate metal carbonyl anions with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide afforded compounds III (58%, orange liquid) and IV (36%, m.p. 21.5–23°C). The chromium analogue II has previously been prepared using a different method [7].

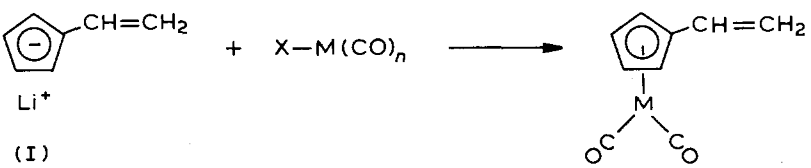


(I)

(III, M = Mo;
IV, M = W)

(II)

Compound I also served as a convenient precursor to a series of (η^5-vinylcyclopentadienyl)dicarbonyl derivatives of cobalt, rhodium, and iridium. The reaction of I with an equimolar mixture of dicobalt octacarbonyl and iodine in THF at 25°C produced V (15%, red-orange liquid) [8]. The reaction of I with $[Rh(CO)_2Cl]_2$ in THF at 25°C, or with $Ir(CO)_3Cl$ in refluxing hexane, afforded monomers VI (47%, orange liquid), and VII (91%, gold liquid), respectively.



(I)

(V, M = Co;
VI, M = Rh;
VII, M = Ir)

TABLE 1

^{1}H NMR COMPARISONS OF (η^5-$C_5H_4CH{=}CH_2$)$M(CO)_2(NO)$ (M = Cr, Mo, W) COMPOUNDS [a]

M	H(3,4)	H(2,5)	H_A	H_B	H_C
Cr (II) [b]	4.92	5.15	6.17	5.32	[c]
Mo (III)	5.52	5.75	6.36	5.45	5.09
W (IV)	5.61	5.82	6.40	5.50	5.17

[a] Recorded in $CDCl_3$ and given in δ ppm units; estimated accuracy ±0.02 ppm. [b] Recorded in $CDCl_3$; see ref. 7. [c] Unresolved, due to overlap with H(3,4) and H(2,5) resonances.

TABLE 2

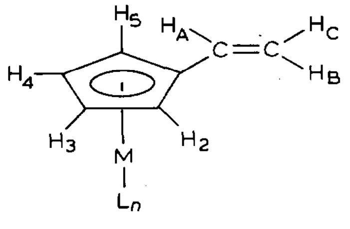
^{1}H NMR COMPARISONS OF (η^5-$C_5H_4CH{=}CH_2$)$M(CO)_2$ (M = Co, Rh, Ir) COMPOUNDS [a]

M	H(3,4)	H(2,5)	H_A	H_B	H_C
Co (V)	5.03	5.25	6.40	5.50	5.02
Rh (VI)	5.45	5.64	6.43	5.49	5.07
Ir (VII)	5.49	5.68	6.46	5.53	5.18

[a] Recorded in $CDCl_3$ and given in δ ppm units; estimated accuracy ±0.02 ppm.

The vinyl derivatives III–VII could be purified by column chromatography on Florisil followed by vacuum distillation.

The ^{1}H NMR spectra for compounds II–IV and V–VII are summarized in Tables 1 and 2, respectively. The proton assignments are indicated in structure VIII. The replacement of a cyclopentadienyl proton with a vinyl group deshields the adjacent protons (H(2) and H(5)) relative to their parent compounds. The vinylmetallocenes and acylmetallocenes of iron, ruthenium, and osmium exhibit a similar deshielding effect [4,6]. Typically, a pair of apparent triplets (A_2B_2 pattern) were observed for protons H(3,4) and H(2,5) in each of the vinyl derivatives.

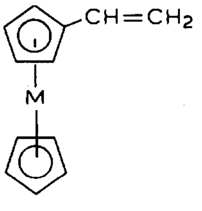


(VIII)

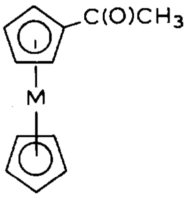
It can be seen from Table 1 that the cyclopentadienyl protons for compounds II–IV occur at lowest field for tungsten, intermediate field for molybdenum, and highest field for chromium. There is a larger difference in chemical shifts between the proton resonances of the chromium compound and the molybdenum compound than between the latter and the tungsten compound. These same trends have also been previously observed for the vinyl- and acyl-metallocenes of iron, ruthenium and osmium (IX–XIV) [4,6].

The vinyl groups in compounds II–IV possess three magnetically non-equivalent protons and can be analyzed for an ABX pattern. The *trans* (*J*(AB)), *cis* (*J*(AC)), and *geminal* (*J*(BC)) coupling constants are approximately 18, 11, and 2 Hz, respectively.

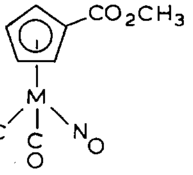
It is interesting to compare the relative chemical shifts for proton H_A as a function of the metal. As can be seen from Table 1, H_A occurs at lowest field for tungsten (δ 6.40), intermediate for molybdenum (δ 6.36), and highest field for chromium (δ 6.17). This trend for proton H_A is in contrast to our earlier findings for vinylosmocene (XI) (δ 6.31), vinylruthenocene (X) (δ 6.34), and vinylferrocene (IX) (δ 6.49), in which the H_A protons exhibit greater shielding in both the ruthenium and osmium derivatives relative to the iron analogue [6]. Protons H_B and H_C are also the most deshielded in the tungsten complex IV, intermediate in the molybdenum derivative III, and least deshielded in the chromium analogue II.



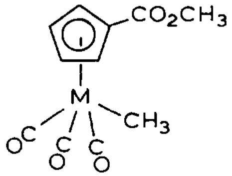
(IX, M = Fe;
X, M = Ru;
XI, M = Os)



(XII, M = Fe;
XIII, M = Ru;
XIV, M = Os)



(XV, M = Cr;
XVI, M = Mo;
XVII, M = W)



(XVIII, M = Cr;
XIX, M = Mo;
XX, M = W)

The chemical shifts of the cyclopentadienyl protons for the cobalt, rhodium, and iridium compounds V–VII show trends similar to those of the chromium, molybdenum, and tungsten compounds II–IV. It can be seen from Table 2 that the cyclopentadienyl protons for compounds V–VII occur at lowest field for iridium, are intermediate for rhodium, and are at highest field for cobalt. Likewise, the chemical shifts of the vinyl protons H_A, H_B, and H_C in compounds V–VII exhibit similar trends to the related protons in II–IV, although the magnitude of the chemical shift differences is not as great. As discussed earlier, [6,9], a variety of factors can affect the chemical shifts of both cyclopentadienyl ring and side-chain protons in a series in which only the central metal atom is varied.

Several of these vinyl organometallic monomers such as III and VII undergo free radical-initiated homo- and co-polymerization to generate the respective metal-containing polymers. Details of these polymerization studies and applications of the resulting polymers will be presented elsewhere.

Conclusions

The new vinyl organometallic monomers II–VII can be prepared in good yields from reactions of vinylcyclopentadienyllithium (I) and appropriate metal carbonyl substrates. The cyclopentadienyl ring protons of II–VII exhibit a gradual deshielding proceeding from the first row (Cr and Co) to the second row (Mo and Rh) to the third row (W and Ir) transition metal. This same trend has been observed for the vinylmetallocenes of iron, ruthenium, and osmium (IX–XI) [6], as well as for the acylmetallocenes of these metals (XII–XIV) [4], and carbomethoxycyclopentadienyl derivatives of chromium, molybdenum and tungsten (XV–XX) [1]. The notable divergence [9] in the relative shielding of the ring and side-chain protons in the substituted iron-group metallocenes (IX–XIV) is not observed in the vinylcyclopentadienylmetal compounds II–IV and V–VII, however.

Experimental

General procedures and materials

All operations were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques. Pentane and hexane were dried over calcium hydride and distilled under argon. Diethyl ether was predried over sodium wire and distilled from sodium benzophenone under argon. Tetrahydrofuran (THF) was predried over KOH and distilled under argon from sodium benzophenone. Diisopropylamine was dried over barium oxide and distilled under nitrogen.

Column chromatography was carried out using Fischer brand Florisil or Alfa-Ventron neutral CAMAG alumina. The Florisil and alumina were heated under vacuum (0.01 mmHg) on a rotary evaporator to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-saturated water.

Chromium, molybdenum, and tungsten hexacarbonyls were obtained from Pressure Chemical Co. Chlorotricarbonyliridium and dicobalt octacarbonyl were obtained from Strem Chemical Co. Dichlorotetracarbonyldirhodium was prepared according to the procedure of McCleverty and Wilkinson [10] as modified by Gardner [11]. 6-(*N,N*-dimethylamino)fulvene was prepared according to Hafner et al. [12].

^{1}H NMR spectra were recorded on a Varian A-60 spectrometer. IR spectra were recorded on either a Perkin–Elmer 237B or a Beckman IR-10 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of 6-methylfulvene

This compound was prepared according to the general method outlined by Hafner and Strum [13]. 6-(*N,N*-Dimethylamino)fulvene (15.0 g, 0.12 mol) was dissolved in ether and 1.3 *M* methyllithium solution (110.1 ml, 0.14 mol) was added dropwise. After the addition was complete, the reaction mixture was refluxed for 5 h and then poured carefully onto ice. The aqueous layer was extracted with ether and the combined organic portions washed with water. The solution was dried over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. The resulting dark residue was placed onto a column of alumina (3 × 60 cm) packed in pentane. Elution of the column with pentane initially gave a brown band which slowly changed into a bright yellow band. The yellow band was collected, and removal of the solvent under vacuum (20 mmHg) gave 5.60 g (51%) of 6-methylfulvene as a gold liquid. The compound was stored under nitrogen at −20°C in the dark. ^{1}H NMR (CCl_4) δ 2.11 (3H, d, CH_3), 6.08–6.67 (5H, m, vinyl).

Preparation of vinylcyclopentadienyllithium (I)

In a 250-ml, three-neck round-bottom flask, equipped with a condenser and nitrogen inlet and outlet valves, were placed diisopropylamine (6.30 ml, 45.0 mmol) and ca. 150 ml of THF. To this was added 1.3 *M* methyllithium (35.0 ml, 45.0 mmol) and the mixture refluxed for 1 h. The solution was cooled to 25°C and 6-methylfulvene (3.90 g, 42.3 mmol) was added. The mixture was stirred for 20 h at 25°C, resulting in a dark brown solution. The THF was then removed under vacuum to give a dark oil. The oil was taken up in ca. 40 ml of ether and ca. 40 ml of pentane was added to produce an off-white solid. This solid was collected under nitrogen and washed with several portions of pentane. The residual pentane was removed under vacuum (0.01 mmHg) to give 4.05 g (98%) of vinylcyclopentadienyllithium as an air-sensitive solid. ^{1}H NMR (THF-d_8) δ 4.27–5.17 (2H, m, $C{=}CH_2$), 5.70 (2H, t, Cp H(3,4)), 5.93 (2H, t, Cp H(2,5)), 6.44–6.90 (1H, q, CH=C).

Preparation of (η^5-vinylcyclopentadienyl)dicarbonylnitrosylmolybdenum (III)

Lithium diisopropylamide was prepared in ca. 100 ml of THF from diisopropylamine (0.76 ml, 5.4 mmol) and 1.1 *M* methyllithium (4.94 ml, 5.4 mmol). To this was added 6-methylfulvene (0.46 g, 5.0 mmol) and the mixture stirred for 20 h at 25°C. Molybdenum hexacarbonyl (1.32 g, 5.0 mmol) was added and the mixture refluxed for 48 h. The solution was cooled to 25°C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (1.05 g, 4.9 mmol) was added, and the mixture stirred for 1 h. The THF was removed under vacuum and the resulting residue extracted with ether. The combined ether extracts were evaporated on Florisil under reduced pressue. The resulting residue was added to a column of Florisil (1.5 × 15 cm) and the column eluted with pentane. An orange band came down the column and was collected under nitrogen. The solvent was removed under vacuum to produce 0.80 g (58%) of (η^5-vinylcyclopentadienyl)dicarbonylnitrosylmolybdenum. An analytical sample was obtained by several recrystallizations from pentane at −78°C followed by molecular distillation to give an orange liquid. (Found: C, 39.57; H, 2.54; N, 5.08. $C_9H_7MoNO_3$ calcd.: C, 39.58; H, 2.58; N, 5.13%). IR (neat) ν(CO) 2010s, 1920s, ν(NO) 1650s cm^{-1}.

Preparation of (η^5-vinylcyclopentadienyl)dicarbonylnitrosyltungsten (IV)

Lithium diisopropylamide was prepared in ca. 100 ml of THF from diisopropylamine (0.47 ml, 3.4 mmol) and 1.1 *M* methyllithium (3.08 ml, 3.4 mmol). To this was added 6-methylfulvene (0.28 g, 3.1 mmol) and the mixture stirred for 20 h at 25°C. Tris(dimethylformamide)tungsten tricarbonyl [14] (1.50 g, 3.1 mmol) was added and the mixture refluxed for 11 h. The solution was cooled to 25°C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.66 g, 3.1 mmol) was added, and the mixture stirred for 1 h. The THF was removed under vacuum and the resulting residue extracted with ether. The combined ether extracts were evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil (1.5 × 15 cm). Elution of the column with pentane produced an orange-brown band which was collected under nitrogen. The solvent was removed under vacuum to give 0.40 g (36%) of (η^5-vinylcyclopentadienyl)dicarbonylnitrosyltungsten as an orange liquid. An analytical sample was obtained by several recrystallizations from pentane at −78°C followed by molecular distillation, m.p. 21.5–23°C. (Found: C, 29.86; H, 1.96; N, 3.93. $C_9H_7NO_3W$ calcd.: C, 29.94; H, 1.95; N, 3.88%). IR (neat) ν(CO) 2000s, 1910s; ν(NO) 1640s cm^{-1}.

Preparation of (η^5-vinylcyclopentadienyl)dicarbonylcobalt (V)

In a 250 ml single-neck round-bottom flask were placed dicobalt octacarbonyl (0.60 g, 1.7 mmol) and 100 ml of THF. To this was added iodine (0.44 g, 1.7 mmol) and the mixture stirred for 1 h at 25°C. Vinylcyclopentadienyllithium (0.34 g, 3.5 mmol) was then added with continued stirring for 12 h. The solvent was removed under vacuum on alumina, and the resulting residue added to a column of alumina (1.5 × 15 cm). Elution of the column with pentane gave a red band which was collected under nitrogen. Removal of the solvent under vacuum gave 0.11 g (15%) of (η^5-vinylcyclopentadienyl)dicarbonylcobalt. This compound was identical to an authentic sample [1].

Preparation of (η^5-vinylcyclopentadienyl)dicarbonylrhodium (VI)

In a 250 ml single-neck round-bottom flask with a side arm were placed dichlorotetracarbonyldirhodium (0.25 g, 0.61 mmol) and ca. 100 ml of THF. The flask was cooled in ice, vinylcyclopentadienyllithium (0.13 g, 1.3 mmol) was added, and the mixture stirred for 2 h. The THF was then evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil (1.5 × 15 cm). Elution of the column with pentane gave an orange band which was collected under nitrogen. The pentane was removed under vacuum to give 0.15 g (47%) of (η^5-vinylcyclopentadienyl)dicarbonylrhodium as an orange liquid. An analytical sample was obtained by molecular distillation. (Found: C, 43.50; H, 2.69. $C_9H_7O_2Rh$ calcd.: C, 43.23; H, 2.82%). IR (neat) ν(CO) 2040s, 1980s cm^{-1}.

Preparation of (η^5-vinylcyclopentadienyl)dicarbonyliridium (VII)

In a 100 ml three-neck round-bottom flask equipped with a condenser and nitrogen inlet and outlet valves were placed vinylcyclopentadienyllithium (1.25 g, 12.7 mmol) and chlorotricarbonyliridium (0.18 g, 0.58 mmol). To this was added ca. 75 ml of hexane and the mixture refluxed for 24 h. The solution was cooled to 25°C under nitrogen and then filtered. The filtrate was evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil (1.5 × 15 cm). Elution of the column with pentane produced a faint yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 0.18 g (91%) of (η^5-vinylcyclopentadienyl)dicarbonyliridium. An analytical sample was obtained by molecular distillation as a yellow liquid. (Found: C, 32.08; H, 2.06. $C_9H_7IrO_2$ calcd.: C, 31.85; H, 2.08%). Ir (neat) ν(CO) 2025s, 1950s cm^{-1}.

Acknowledgement

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