Pentacarbonyl(η^2-vinylferrocene)metal(0) complexes of Group 6 elements: synthesis and characterization

Saim Özkar *, Ceyhan Kayran, Nazlan Demir

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

Abstract

Photolysis of hexacarbonylmetal(0) complexes of the Group 6 elements in the presence of vinylferrocene in an n-hexane solution at $-15\,^\circ$C yields pentacarbonyl (η^2-vinylferrocene)metal(0) complexes as the sole photo-substitution product, different from the general reaction pattern observed for the same Group 6 metal carbonyls with other olefins. $M(CO)_5(\eta^2$-vinylferrocene) complexes (M = Cr, Mo, W) could be isolated from the solution and characterized by using spectroscopic techniques. The complexes were found to be not very stable and their stability increases in the order Cr < Mo < W. The relatively stable $W(CO)_5(\eta^2$-vinylferrocene) could be isolated as a pure solid and characterized by elemental analysis, MS, IR and NMR spectroscopy, while the solid samples of the less stable $Cr(CO)_5(\eta^2$-vinylferrocene) and $Mo(CO)_5(\eta^2$-vinylferrocene) complexes were found to be contaminated with free vinylferrocene and characterized only by using IR and NMR spectroscopy.
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1. Introduction

Olefin-substituted Group 6 metal carbonyls are conveniently accessible from the parent $M(CO)_6$ complexes (M = Cr, Mo, W) by means of photolytic CO detachment in the presence of the appropriate olefin. This has been demonstrated using ethene and linear alkenes [1–5], cyclooalkenes [5–7], α,β-unsaturated esters [8], and tetracyanoethene [9] as the entering ligand. These olefin-substituted metal carbonyls are relevant to the homogeneous photocatalytic processes [10] such as isomerization [11], hydrogenation [12], and hydrosilylation [13] of mono- and diolefins. A recent kinetic study [14] on the photochemical conversion of $W(CO)_6$ into a *trans*-$W(CO)_4(\eta^2$-olefin)$_2$ complex using E-cyclooctene as a model olefin owing to its extraordinary coordination properties [15] showed that the photolysis of $M(CO)_6$ in the presence of an olefin is expected to yield the stable final product *trans*-$M(CO)_4(\eta^2$-olefin)$_2$ through the intermediate $M(CO)_5(\eta^2$-olefin) and *cis*-$M(CO)_4(\eta^2$-olefin)$_2$ complexes as shown in Scheme 1. Indeed, with the exception of tetracyanoethylene [9] and Z-cyclooctene for the case of chromium [6], *trans*-$M(CO)_4(\eta^2$-olefin)$_2$ is always found to be the final product of the photosubstitution of CO in the Group 6 metal carbonyls in the presence of excess olefin. In the case of tetracyanoethene [9] and Z-cyclooctene with chromium [6], the photosubstitution stops at the first step, forming $M(CO)_5(\eta^2$-olefin). Here we report the photolysis of the Group 6 hexacarbonylmetal(0) complexes in the presence of vinylferrocene, an olefin bearing the ferrocene moiety. Photo-substitution yields only pentacarbonyl(η^2-vinylferrocene)metal(0) as the final product, which were isolated from the reaction solution and characterized by using IR, MS and NMR spectroscopy and elemental analysis.

Ferrocene [16] has been used in the synthesis of many new materials having interesting properties [17,18]. For instance, molecules containing ferrocene moiety have been used as homogeneous catalysts [18], molecular sensors [19], molecular magnets [20], non-linear optic materials [21], and liquid crystals [22]. The presence of ferrocene in a molecule is expected to influence its

* Corresponding author. Tel.: +90-312-210-3212; fax: +90-312-210-1280.
 E-mail address: sozkar@metu.edu.tr (S. Özkar).
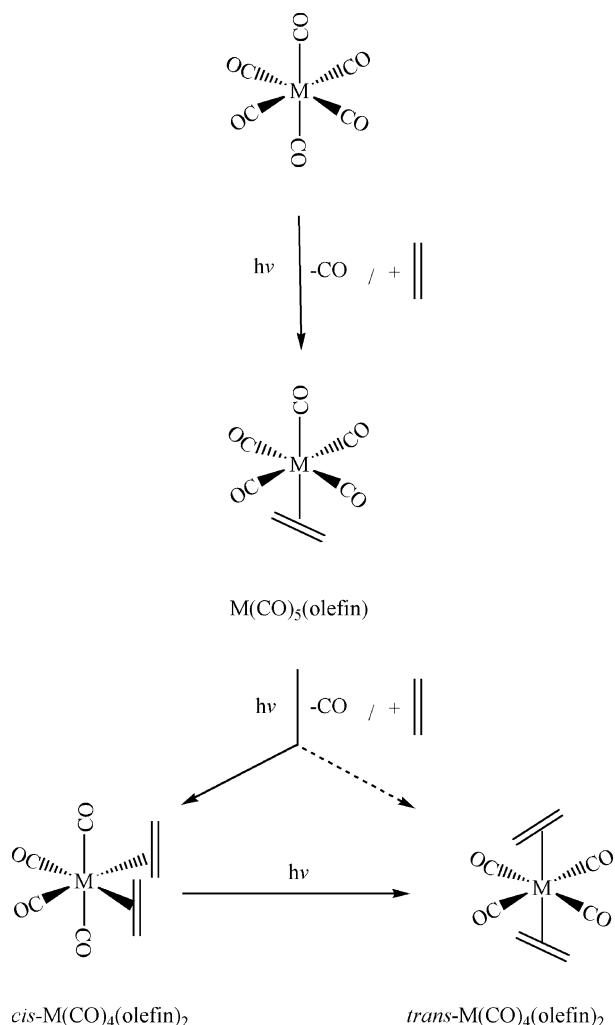
Scheme 1. CO substitution reaction in the photolysis of hexacarbonylmetal(0) in the presence of olefin.

electron transfer ability [23]. Thus, vinylferrocene [24] has been used in preparing polymeric materials having interesting electronic and redox properties [25]. However, vinylferrocene has not been used as an olefin ligand yet. The pentacarbonyl(η^2-vinylferrocene)metal(0) complexes are the first examples of transition metal complexes containing vinylferrocene as an olefin ligand.

2. Experimental

2.1. General remarks

All reactions and manipulations were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used.

Analytical grade and deuterated solvents, hexacarbonylchromium(0), hexacarbonylmolybdenum(0), and hexacarbonyltungsten(0) were purchased from Aldrich Chemical Co. Ltd., Dorset, UK, and vinylferrocene was granted by Chemische Betriebe Pluto GmbH, Herne, Germany, and used as received. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra from solutions on a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for ^{1}H; and 100.6 MHz for ^{13}C spectrometer). TMS was used as internal reference for ^{1}H- and ^{13}C-NMR chemical shifts. Mass spectra were taken on a Finnigan MAT 8400 instrument. UV–Vis electronic absorption spectra were taken on a HP 8453 diode array spectrophotometer. Elemental analyses were performed on a LECO CHNS-932 instrument.

Photochemical reactions were carried out in an immersion-well apparatus [26] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating water or cold methanol.

2.2. $W(CO)_5(\eta^2$-vinylferrocene) (3)

A solution of 1.0 g (2.8 mmol) $W(CO)_6$ and 0.60 g (2.8 mmol) vinylferrocene in n-hexane (200 ml) was irradiated at $-15\ ^\circ$C until the starting material was no longer observed in the IR spectrum (ca. 20 h). Upon reducing the volume to ca. 5 ml and cooling the solution to $-78\ ^\circ$C orange crystals of 3 precipitated (0.66 g, 44% yield). Traces of unreacted vinylferrocene and hexacarbonyltungsten(0) were sublimed out in vacuum on a coldfinger at $-30\ ^\circ$C while keeping the complex at $0\ ^\circ$C in an ice bath: m.p. 65 $^\circ$C (dec); IR (n-hexane): ν(CO) 2078.8, 1995.8, 1962.9, 1951.8, 1945.4 cm^{-1}; UV–Vis (n-hexane) $\lambda_{max} = 274$ (3170), 320 (1360), 450 (96) nm ($\varepsilon = 1$ mol^{-1} cm^{-1}); ^{13}C-{^{1}H}-NMR (toluene-d_8) $\delta = 202.12$ (CO$_{trans}$), 196.55 (CO$_{cis}$), 89.63 (C6), 85.50 (C1), 69,52 (C1′–C5′), 69.21 (C2, C5), 62.86 (C3, C4), 55.70 (C7) ppm; ^{1}H-NMR (toluene-d_8) $\delta = 5.24$ (H6), 4.07 (H2, H5), 3.92 (H3, H4), 3.78 (H1′–H5′), 3.34 (H7′), 2.86 (H7) ppm, $J_{H6-H7} = 9.0$, $J_{H6-H7'} = 14.8$ Hz; MS $m/z = 536$ [M$^+$]; CV(CH$_2$Cl$_2$) ox. pot = 0.81 (rev), 1.52V, red. pot = -0.86 (irrev) V. Anal. Calc. for C$_{17}$H$_{12}$O$_5$WFe (M = 535.99): C, 38.09; H, 2.26; Found: C, 38.35; H, 2.29%.

2.3. $Mo(CO)_5(\eta^2$-vinylferrocene) (2)

A solution of 1.0 g (3.8 mmol) Mo(CO)$_6$ and 0.80 g (3.8 mmol) vinylferrocene in n-hexane (200 ml) was irradiated at $-15\ ^\circ$C until the starting material was no longer observed in the IR spectrum (ca. 20 h). Upon reducing the volume to ca. 5 ml and cooling the solution

to $-78\ ^\circ$C orange crystals of **2** precipitated (0.28 g, 16% yield). Unreacted vinylferrocene and hexacarbonylmolybdenum(0) were sublimed out in vacuum on a coldfinger at $-30\ ^\circ$C while keeping the complex at $0\ ^\circ$C in an ice bath. However, traces of free vinylferrocene remained in the solid substance: m.p. $55\ ^\circ$C (dec); IR (n-hexane) $v(CO) = 2079.3, 1997.5, 1965.3, 1959.0, 1945.4\ \text{cm}^{-1}$; $^{13}C-\{^1H\}$-NMR (toluene-d_8) $\delta = 213.45$ (CO_{trans}), 204.57 (CO_{cis}), 97.57 (C6), 84.11 (C1), 70.27 (C1′–C5′), 66.8 (C2, C5), 63.15 (C3, C4), 62.57 (C7) ppm, ^1H-NMR (toluene-d_8) $\delta = 5.25$ (H6), 4.43 (H2, H5), 4.12 (H3, H4), 3.85 (H1′–H5′), 3.43 (H7′), 2.92 (H7)ppm, $J_{H6-H7} = 9.2$, $J_{H6-H7'} = 15.2$ Hz.

2.4. $Cr(CO)_5(\eta^2\text{-vinylferrocene})$ (1)

A solution of 1.0 g (4.5 mmol) $Cr(CO)_6$ and 0.96 g (4.5 mmol) vinylferrocene in n-hexane (200 ml) was irradiated at $-15\ ^\circ$C until the starting material was no longer observed in the IR spectrum (ca. 20 h). Upon reducing the volume to ca. 5 ml and cooling the solution to $-78\ ^\circ$C orange crystals of **1** precipitated (0.22 g, 12% yield). Unreacted hexacarbonylchromium(0) was sublimed out in vacuum on a coldfinger at $-30\ ^\circ$C while keeping the complex at $0\ ^\circ$C in an ice bath. However, free vinylferrocene could not be removed completely: m.p. $55\ ^\circ$C (dec); IR(n-hexane) $v(CO) = 2070.8, 1992.9, 1957.1, 1946.5\ \text{cm}^{-1}$; $^{13}C-\{^1H\}$-NMR (toluene-d_8) $\delta = 221.73$ (CO_{trans}), 216.14 (CO_{cis}), 89.20 (C6), 85.03 (C1), 69.67 (C1′–C5′), 66.56 (C2, C5), 62.45 (C3, C4), 55.31 (C7) ppm; ^1H-NMR (toluene-d_8) $\delta = 4.92$ (H6), 3.96 (H2, H5), 3.84 (H3, H4), 3.71 (H1′–H5′), 3.16 (H7′), 2.68 (H7) ppm, $J_{H6-H7} = 8.9$, $J_{H6-H7'} = 14.8$ Hz.

3. Results and discussion

Irradiation of $M(CO)_6$ (M = Cr, Mo, W) in the presence of vinylferrocene (vfc) in n-hexane at $-15\ ^\circ$C results in nearly complete conversion into $M(CO)_5(\eta^2\text{-vfc})$ (**1–3**), Scheme 2, which are isolated and characterized by elemental analysis (for M = W), MS, UV–vis, IR, ^1H- and ^{13}C-NMR spectroscopy.

The IR spectrum of **3**, for example, exhibits four prominent bands at 2078.8, 1962.9, 1951.8 and 1945.4 cm^{-1} in the CO stretching vibrational region along with a weak absorption at 1995.8 cm^{-1} (Fig. 1). The five-band $v(CO)$ pattern indicates that the C_{4v} symmetry of $M(CO)_5$ skeleton, commonly observed for $M(CO)_5L$ complexes [$v(CO)$ modes: $2A_1$, E (IR active) and A_2 (IR inactive)] [27], is reduced to C_{2v} symmetry by the single-face π acceptor character of the alkene ligand, by disregarding the substituent effect on its symmetry: the degeneracy of the very intense E mode is lifted ($\rightarrow B_1$, B_2) and the A_2 becomes IR active ($\rightarrow B_1$), albeit with intrinsically low intensity, such that the assignments of
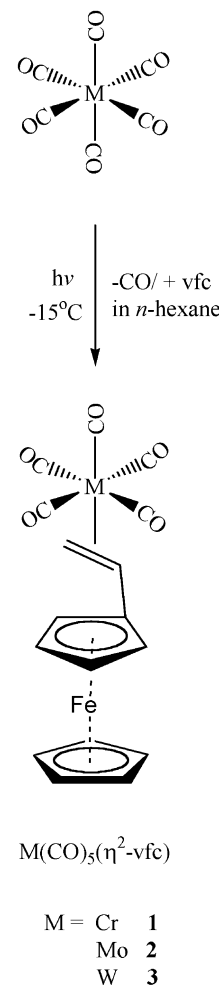
Scheme 2. CO substitution reaction in the photolysis of $M(CO)_6$ in the presence of vinylferrocene (vfc).

bands in Fig. 1 is straightforward. The two strongest bands in the spectrum apparently correspond to the two components of the very intense E mode under C_{4v} symmetry and thus are assigned as the B modes of **3**.

The IR spectra of the other two complexes exhibit essentially the same $v(CO)$ absorption pattern as the one observed for **3** (Fig. 1). The absorption frequencies of all the three $M(CO)_5(\eta^2\text{-vfc})$ complexes are listed in Table 1. One remarkable observation in the carbonyl stretching spectra of the three complexes is that the frequency separation between the $B_1^{(2)}$ and B_2 bands gradually decreases on going from tungsten to chromium. In other words, the two bands appear to be separated in the tungsten complex by 11.1 cm^{-1} (1962.9–1951.8 = 11.1 cm^{-1}), moderately separated in the molybdenum complex 6.3 cm^{-1} (1965.3–1959.0 = 6.3 cm^{-1}), and overlapped in the chromium complex (1957.1–1957.1 = 0 cm^{-1}). This trend reflects the increase in the discriminating influence of olefin on the two pairs of equatorial carbonyls as the size of the metal increases. Both the principal force constants and the interaction constants may become different, but it is mainly the increasing
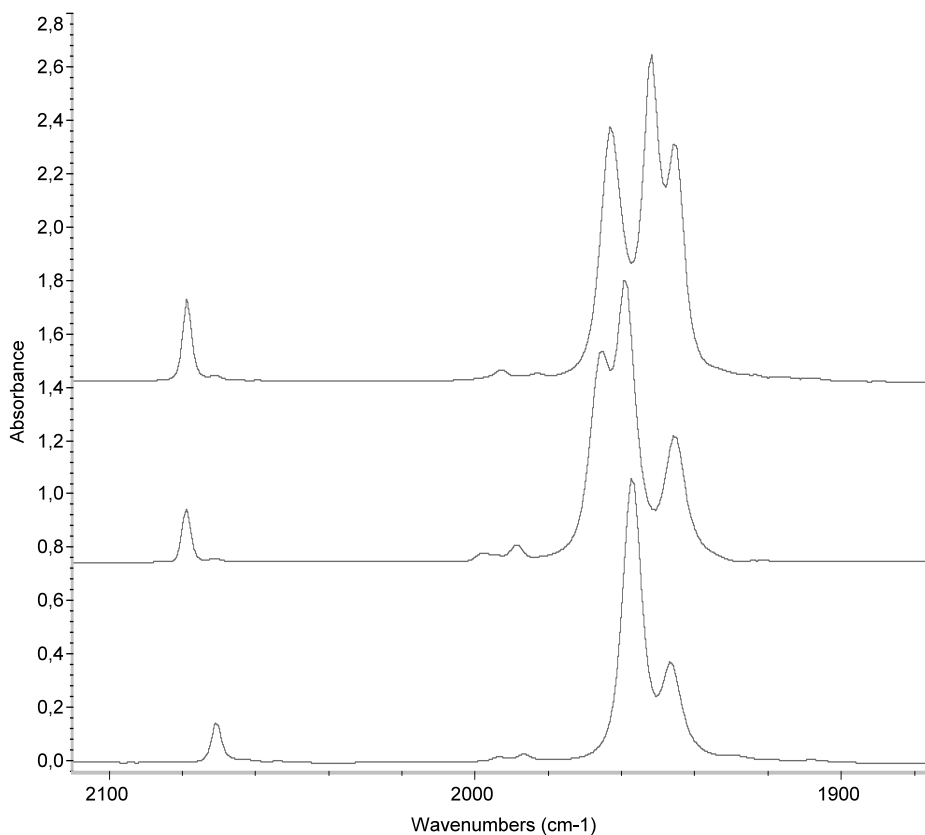
Fig. 1. IR spectra of **1** (bottom), **2** (middle) and **3** (top) in the ν(CO) region recorded in *n*-hexane.

difference of the principal force constants, not the interaction constants, which dominates the effect.

The ^{13}C-NMR spectra of the complexes exhibit two lines for the carbonyl groups in an approximately 1:4 intensity ratio, two lines for the olefinic carbon atoms, and four lines for the ferrocenyl moiety (Table 2). The appearance of only one signal for the four equatorial CO groups indicates that the molecule is fluxional with respect to rotation about the metal–alkene bond axis. Vinyl carbons show a significant coordination shift: $\Delta\delta = 55.41$, 48.15 and 55.02 ppm for the terminal carbon C7, and $\Delta\delta = 45.84$, 37.47 and 45.41 ppm for the vinylic carbon C6 in the chromium, molybdenum, and tungsten complexes, respectively. The signals of the cyclopentadienyl ring carbons show only slight changes upon coordination to the Group 6 metal through the vinyl C=C bond.

In the ^{1}H-NMR spectra, the complexes give three doublets for the olefinic hydrogen atoms, two singlets for the substituted and one singlet for the unsubstituted cyclopentadienyl ring hydrogen atoms (Table 3). The appearance of all the signals of olefinic hydrogens as doublets indicates that the coupling constant between the geminal protons is small ($J_{H7-H7'} < 1$), while the *cis* and *trans* vicinal coupling constants (J_{H6-H7} and $J_{H6-H7'}$) are large, albeit slightly reduced upon coordination (Table 3). The olefinic hydrogen atoms also show coordination shifts in the range of 1–2 ppm, while the cyclopentadienyl ring protons experience only slight changes upon coordination (Table 3).

Photolysis of an *n*-hexane solution of hexacarbonyl-metal(0) in the presence of vinylferrocene gives only the monosubstitution product for all of the three metals, chromium, molybdenum, and tungsten, as shown in

Table 1
CO stretching frequencies, ν(CO) in cm^{-1}, of the M(CO)$_5$(η^2-vfc) complexes in *n*-hexane at room temperature

M(CO)$_5$(η^2-vfc)	Nr	ν(CO) cm^{-1}				
		$A_1^{(1)}$	$B_1^{(1)}$	$B_1^{(2)}$	B_2	$A_1^{(2)}$
Cr	**1**	2070.8	1992.9	1957.1	1957.1	1946.5
Mo	**2**	2079.0	1997.5	1965.3	1959.0	1945.4
W	**3**	2078.8	1995.8	1962.9	1951.8	1945.4

Table 2

^{13}C-NMR chemical shift (δ in ppm, rel. to TMS) of vinylferrocene (vfc) and the M(CO)$_5$(η^2-vfc) complexes **1**–**3** in toluene-d_8, coordination shifts are given in parentheses
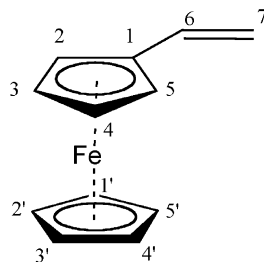
	δ (ppm)							
	CO$_{trans}$	CO$_{cis}$	C7	C6	C1	C2, C5	C3, C4	C1′–C5′
vfc			110.72	135.04	83.51	68.60	67.55	69.82
1	221.73	216.14	55.31 (55.41)	89.20 (45.84)	85.03	66.56	62.45	69.67
2	213.45	204.57	62.57 (48.15)	97.57 (37.47)	84.11	66.80	63.15	70.27
3	202.12	196.55	55.70 (55.02)	89.63 (45.41)	85.50	69.21	62.86	69.52

Table 3

^{1}H-NMR chemical shift (δ in ppm, rel. to TMS) and coupling constant (in Hz) of vinylferrocene (vfc) and the M(CO)$_5$(η^2-vfc) complexes **1**–**3** in toluene-d_8, coordination shifts are given in parentheses

	δ (ppm) and J (Hz)								
	H7	H7′	H6	H2, H5	H3, H4	H1′–H5′	J_{H6-H7}	$J_{H6-H7'}$	$J_{H7-H7'}$
vfc	5.02	5.36	6.47	4.08	3.81	3.74	10.2	17.3	1.4
1	2.68	3.16	4.92	3.96	3.84	3.71	8.9	14.8	<1
2	2.92	3.43	5.25	4.43	4.12	3.85	9.2	15.2	<1
3	2.86	3.34	5.24	4.07	3.92	3.78	9.0	14.8	<1

Scheme 2. The photosubstitution of one CO group in M(CO)$_6$ by vinylferrocene is the sole reaction in this photolysis and continues practically until the complete conversion of M(CO)$_6$ to the mono-substitution product. Prolonged irradiation of the solution does not give any further CO substitution; it causes rather M(CO)$_5$(η^2-vfc) to decompose very slowly. That photo-substitution reaction does not go beyond the monosub-stitution can be ascribed to the strengthening of the M–CO bonds by CO replacement with vinylferrocene. Indeed, the CO stretching frequencies in the M(CO)$_5$(η^2-vfc) complexes are much smaller than those in the similar M(CO)$_5$(η^2-olefin) complexes (e.g. ethyl-ene [28], *E*-cyclooctene [10]). Thus, the M–CO bonds in M(CO)$_5$(η^2-vfc) are expected to be stronger than those in the other M(CO)$_5$(η^2-olefin) complexes, which un-dergo the second CO substitution upon further irradia-tion [16].

These three complexes differ markedly in their stability and, therefore, ease of isolation. Of the three, only W(CO)$_5$(η^2-vfc) could be isolated as a pure solid substance, while the Mo(CO)$_5$(vfc) and Cr(CO)$_5$(η^2-vfc) were obtained in the solid state contaminated with free vinylferrocene. The presence of free vinylferrocene is attributed to the decomposition of the complexes during the isolation process. Also Mo(CO)$_6$ or Cr(CO)$_6$ are formed concomitantly together with the free vinylferro-cene. However, the volatile Mo(CO)$_6$ or Cr(CO)$_6$ could easily be removed by sublimation in vacuum. The instability of the complexes may be due to the fact that the C=C double bond of vinylferrocene is highly activated upon coordination to the transition metal and, thus more readily susceptible to polymerization reac-tions. In fact, during handling the complexes undergo some decomposition, ending up with the formation of black polymeric materials.

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