

SUPPORTED CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES

II *. POLYSTYRENE-SUPPORTED CARBONYL AND NITROSYL DERIVATIVES OF GROUP VI TRANSITION METALS

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Summary

Tricarbonyl hydride derivatives of cyclopentadienyl-chromium, -molybdenum and -tungsten compounds covalently linked to a macroreticular polystyrene support are obtained by treatment of polystyrene-attached cyclopentadienyl anions with the respective metal hexacarbonyl and subsequent acidification. In contrast to the ease with which unsupported cyclopentadienyl-chromium and -molybdenum tricarbonyl hydrides lose H_2 to form dinuclear carbonyl species, no H_2 is released from their polymer-supported counterparts below about $180^\circ C$, and no dinuclear species are detectable after partial thermal decomposition at higher temperatures. The identity of the polymer-supported chromium species is confirmed by its conversion into nitrosyl derivatives.

Introduction

The reaction patterns of polymer-supported organometallic compounds and their potential applications in catalytic processes are receiving much attention at present, and we recently initiated a study on polymer-supported cyclopentadienylmetal carbonyl compounds [1]. This class of compounds is particularly suitable for an investigation of fundamental structures and modes of reaction because of the easily detectable IR spectra, restricted structural parameters of these half-sandwich derivatives and the availability of data on the homogeneous reference systems. We describe below the synthesis and characterization of cyclopentadienyl-chromium, -molybdenum and -tungsten derivatives covalently

* For part I see ref. 1.

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linked to a macroreticular, cross-linked polystyrene-18% divinylbenzene copolymer.

Results and discussion

1. Synthesis and characterization of chromium, molybdenum and tungsten tricarbonyl hydride derivatives

Group VI transition metal tricarbonyl species are introduced to a polymer network by treatment of polystyrylmethylenecyclopentadienyl* anion, [2] (PS)—CH₂—C₅H₄⁻, containing about 1.5 mmol C₅H₄⁻ per g of polymer, with chromium, molybdenum or tungsten hexacarbonyl, in dimethyl formamide at 130°C [3], subsequent removal of excess hexacarbonyl, and acidification with acetic acid.

The yellowish tungsten compound obtained after reaction for 4 h contained 0.94% tungsten; corresponding to 0.051 mmol W per g of polymer or about one cyclopentadienyltungsten unit per 200 styryl units. By extending the reaction time to 24 h, a tungsten contents of up to 5% can be obtained, corresponding to 0.25 mmol W per g of polymer or about one cyclopentadienyltungsten unit per 40 styryl units.

Upon heating to temperatures of 200–220°C, these materials release 2.95 ± 0.05 mmol CO and 0.45 ± 0.05 mmol H₂ per mmol W present, and the IR spectra of the thermolysis products show no carbonyl bands. The results are consistent with the expected composition (PS)—CH₂—C₅H₄W(CO)₃H. This assignment is further supported by IR spectral data: two strong, terminal CO-absorption bands** of the polymer-supported material at 2020 and 1920 cm⁻¹ are almost indistinguishable in position and relative intensity from those of C₅H₅W(CO)₃H [4]. Similar spectra, resembling those of C₅H₅M(CO)₃H derivatives, are obtained for the corresponding chromium and molybdenum compounds (Table 1). The molybdenum derivative is formed by substitution of Mo(CO)₆ faster than the derivatives of the other two metals and a molybdenum content of 4.5% (4.7 mmol Mo per g of polymer or about one cyclopentadienylmolybdenum unit per 20 styryl units) is obtained after only 4 h. An increased reactivity of Mo(CO)₆ in comparison to Cr(CO)₆ and W(CO)₆ has been observed by Fischer et al. [3] in related substitution reactions with C₅H₅⁻. The polymer-supported metal compounds were further characterized by thermoanalytical studies. The materials undergo endothermic decompositions with loss of H₂ and CO at temperatures of about 200–210°C. Loss of C₅H₅ and C₅H₆ is observed at 170–230°C.

The thermal stability of the polymer-supported cyclopentadienylmetal tricarbonyl hydrides, particularly those of chromium and molybdenum, up to temperatures close to the melting points of the polymer matrix contrasts sharply with the thermal instability of C₅H₅Cr(CO)₃H and C₅H₅Mo(CO)₃H. These compounds are known to lose H₂ at temperatures of about 50°C with formation of

* (PS) = polystyryl.

** IR absorptions due to M—H vibrations cannot be distinguished from background absorptions in these polymeric materials; they are reported to be relatively weak in the analogous compounds C₅H₅M(CO)₃H [6].

TABLE 1
IR ABSORPTION DATA IN THE $\nu(\text{CO})$ ABSORPTION RANGE (in cm^{-1})

	$(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{M}(\text{CO})_3\text{H}$	$\text{C}_5\text{H}_5\text{M}(\text{CO})_3\text{H}$ (ref. 4,5)
Cr	2020, 1920	2018, 1934, 1908, 1888
Mo	2030, 1930	2030, 1949, 1913w
W	2020, 1925	2020, 1929, 1980w

the binuclear species $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ [3]. The dinuclear molybdenum and tungsten compounds are readily distinguished from their mononuclear tricarbonyl hydride precursors by their characteristic IR spectra [7–9]. No absorption bands assignable to such a dimer are observed, however, when IR spectra of the polymer-supported tricarbonyl hydride compounds are monitored during their thermolysis. Instead, the frequencies of their CO absorption bands remain unchanged while these bands disappear gradually and simultaneously. We conclude, therefore, that the mutual isolation of the cyclopentadienylmetal centers by their attachment to a rigid, cross-linked polymer matrix, at the relatively low degrees of substitution present, precludes metal–metal interactions except for a negligible statistical fraction of the metal centers present. The very great retardation of the thermal release of H_2 from the polymer-supported tricarbonyl hydride derivatives compared with that from the unsupported analogues accordingly indicates that the rate-determining step of the normal H_2 evolution in homogeneous solution involves a binuclear species which is not available for the polymer-supported compound. This would exclude, e.g., a monomolecular, homolytic cleavage of thermal Mo–H bond with formation of radical species as the rate-determining step of the H_2 evolution in homogeneous solution.

For $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$, a photoinduced dimerisation has also been reported [3]. UV-irradiation of $(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{W}(\text{CO})_3\text{H}$ does not cause spectral changes which could be ascribed to a polymer-bound analogue of $[\text{C}_5\text{H}_5\text{W}(\text{CO})_3]_2$; an unidentified species with IR absorptions at 1920 and 1850 cm^{-1} appears as an intermediate after partial photolysis.

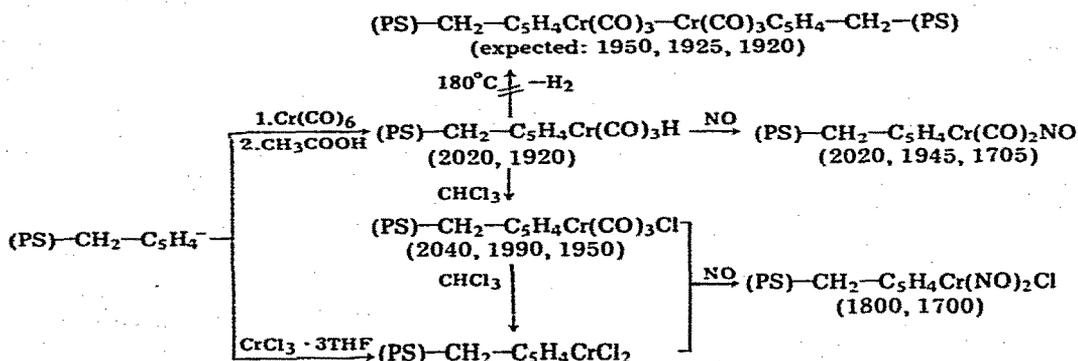
2. Nitrosyl derivatives

We have further characterized the polymer-supported compounds described above and extended their reaction patterns by converting them to other species with characteristic, easily identifiable IR spectra, especially nitrosyl derivatives.

Reaction of $(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{Cr}(\text{CO})_3\text{H}$ with NO in dioxane/water leads to a yellow product with IR absorptions at 2020 and 1945 cm^{-1} ($\nu(\text{CO})$) and an additional band at 1705 cm^{-1} ($\nu(\text{NO})$). The close agreement of these spectral data with those reported for $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})_2\text{NO}$ [10,11] indicate that the mixed carbonyl nitrosyl derivative $(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{Cr}(\text{CO})_2\text{NO}$ is formed.

When the tricarbonyl hydride is first converted into a chloride-containing species the reaction with NO takes a different course. When $(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{Cr}(\text{CO})_3\text{H}$ is heated in chloroform, one observes the intermediary formation of a derivative with weak IR absorptions at 2040, 1990 and 1950 cm^{-1} . Comparison with IR data given for $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{X}$ derivatives (X = halogen) [12], indicates that $(\text{PS})-\text{CH}_2-\text{C}_5\text{H}_4\text{Cr}(\text{CO})_3\text{Cl}$ is formed. Continued treatment with CHCl_3

SCHEME 1. Reaction scheme of polystyrylmethylenecyclopentadienylchromium derivatives. (Numbers in parentheses indicate characteristic IR absorption frequencies in cm^{-1} .)



converts this material to another chloride derivative showing no CO bands, presumably $(\text{PS})\text{-CH}_2\text{-C}_5\text{H}_4\text{CrCl}_2$ (vide infra). Introduction of NO into the reaction mixture in CHCl_3 leads, over a period of about 24 h, to a green material, characterised as $(\text{PS})\text{-CH}_2\text{-C}_5\text{H}_4\text{Cr}(\text{NO})_2\text{Cl}$ by two NO absorption bands at 1800 and 1700 cm^{-1} , which are in close agreement with those reported for $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ [13]. The identity of this material is further supported by its formation by an alternative synthetic route. In this, treatment of cyclopentadienyl anion with $\text{CrCl}_3 \cdot 3\text{THF}$ leads to $(\text{PS})\text{-CH}_2\text{-C}_5\text{H}_4\text{CrCl}_2$ and reaction of this compound with NO gives the compound $(\text{PS})\text{-CH}_2\text{-C}_5\text{H}_4\text{Cr}(\text{NO})_2\text{Cl}$ as in the corresponding homogeneous reaction [13].

The data summarised in the Scheme 1 support the identity of the materials obtained and substantiate the view that the reaction modes of the polystyrene-supported cyclopentadienylmetal compounds largely parallel those of corresponding species in homogeneous solution as long as the reactions can proceed at isolated metal centers.

Material

Procedures

All reactions were carried out with exclusion of air, either in Schlenk equipment or on a vacuum manifold. Solvents were dried with LiAlH_4 or P_4O_{10} and distilled on a vacuum manifold immediately prior to use. Transfer of solid samples was performed in a nitrogen-filled glove box. Samples for IR spectra were prepared by crushing the polystyrene beads in an agate mortar under N_2 and mulling a weighed amount of 10–15 mg of the pulverised material with 0.5 ml of air-free Nujol; spectra were then recorded in demountable NaCl cells with a 0.25 mm Teflon spacer.

For the analysis of chromium and of metal-bound chlorine, weighed samples of the polymer materials were treated with 15 ml of 2 M NaOH or KOH for 24 h at 80°C and, in the case of Cr analysis, with 15 ml of 30% H_2O_2 . After dilution, chromium was determined as CrO_4^{2-} by spectrophotometric or iodometric meth-

ods and chloride by potentiometric titration with AgNO_3 . Molybdenum and tungsten analysis were performed by Alfred Bernhard, Microanalytical Laboratories, 5251 Elbach BRD. For determination of the amount of evolved CO and H_2 , weighed samples of the polymeric materials were slowly heated to temperatures up to 220°C for periods up to 6 h in a Schlenk vessel connected to a vacuum manifold. Non-condensable gases were collected in a Toepler pump. After gas-volumetric determination of the sum of CO and H_2 , the mixture was converted into CO_2 and H_2O by passage through a CuO tube at 310°C and the amount of CO_2 measured separately.

Thermoanalytic analyses were performed on a Netzsch 429 Thermoanalyzer, which permits simultaneous recording of weight and enthalpy changes and mass spectral analysis of gaseous products.

Polystyrylmethylenecyclopentadiene

Preparations were carried out as described in the literature [2,14,15]. As support material, beads (0.5–0.7 mm diameter) of a macroreticular styrene-18%-divinyl benzene copolymer with pore diameters of 250–350 Å was used, which was obtained as a gift from Bayer AG. The Cl contents [15] after chloromethylation were 1.4–1.8 mmol Cl/g polymer. Substitution with a three to four-fold excess of $\text{C}_5\text{H}_5\text{Na}$ was carried out in refluxing tetrahydrofuran for two days; after this, the Cl content of the polymer was below 0.05 mmol Cl/g polymer. After washing with methanol and tetrahydrofuran to remove all NaCl, the materials were dried at 10^{-3} torr and room temperature for several days.

The C_5H_5 content of the products was determined by reaction with a two- to three-fold excess of CH_3Li in tetrahydrofuran for three to four days and gas-volumetric determination of the amount of CH_4 formed. The C_5H_5 contents thus determined are in close agreement with the difference between the Cl contents before and after reaction with $\text{C}_5\text{H}_5\text{Na}$.

Polystyrylmethylenecyclopentadienylmetal tricarbonyl hydrides

A 5 g sample of the cyclopentadiene-substituted polymer (1.42 mmol $\text{C}_5\text{H}_5/\text{g}$ polymer) was converted into the lithium salt as described in ref. 2; 1.6 g $\text{Cr}(\text{CO})_6$ (7 mmol) and 60 ml of dry dimethyl formamide were added and the mixture was heated to 130°C for 5 h. After cooling to room temperature, the polymer was collected by filtration and washed with dry dimethyl formamide until the filtrate was free of carbonyl absorptions, and with ether to remove the dimethyl formamide. The material was then treated with 50 ml of a 2 M solution of acetic acid in a 1/1 mixture of water and dioxane, filtered, washed neutral with water/dioxane, with dioxane and finally with diethyl ether. The yellowish material was then dried at 10^{-3} torr and room temperature for two days.

The chromium content of this material was 1.55%, IR absorptions at 2020 and 1920 cm^{-1} are in close agreement with those of $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$ (Table 1). No absorptions assignable to arenometal tricarbonyl species [16] are present in the IR spectra of these compounds.

Molybdenum and tungsten derivatives were prepared analogously.

Photolysis of polystyrylmethylenecyclopentadienyltungsten tricarbonyl hydride

A 200 mg sample of the crushed polymer-supported tricarbonyl hydride deri-

vative was stirred with 8 ml n-heptane in a quartz test tube with exclusion of air, and the mixture was irradiated at room temperature with light from a 125 W high-pressure mercury lamp while a slow stream of argon saturated with n-heptane vapor was passed through the suspension. At regular intervals samples of the polymer were removed and dried, and their IR spectra recorded.

Reaction of polystyrylmethylenecyclopentadienylchromium tricarbonyl hydride with CHCl_3 and NO

A 0.5 g sample of the tricarbonyl hydride derivative was stirred in 10 ml of dry CHCl_3 for 24 h. The IR spectrum of the product still showed absorptions at 2020 and 1920 cm^{-1} due to the starting material; three weak bands at 2040, 1990 and 1950 cm^{-1} indicate partial formation of a tricarbonyl chloride derivative. Continued treatment with CHCl_3 at reflux temperature caused complete disappearance, first of the bands at 2020 and 1900 cm^{-1} and then of all absorptions in the CO region. NO was then introduced and the mixture was stirred for 24 h at room temperature to give a yellow material with $\nu(\text{NO})$ absorptions at 1800 and 1700 cm^{-1} , indicative of the presence of a dinitrosyl chloride derivative.

Polystyrylmethylenecyclopentadienylchromium dichloride

Cyclopentadiene-substituted polymer (5.3 g; 1.8 mmol $\text{C}_5\text{H}_5/\text{g}$ polymer) was converted into the lithium salt and treated with 4.4 g $\text{CrCl}_3 \cdot 3\text{THF}$ (11.8 mmol) in tetrahydrofuran at room temperature for several days. The solid was filtered off and extracted with tetrahydrofuran in a Soxhlet apparatus overnight. The blue-green material was dried at 10^{-3} torr and room temperature for two days. A chromium content of 0.70 mmol Cr/g and a chlorine content of 1.47 mmol Cl/g indicate the presence of $\text{C}_5\text{H}_4\text{CrCl}_2$ groups.

Polystyrylmethylenecyclopentadienylchromium dinitrosyl chloride

A 0.8 g sample of the polymer-supported cyclopentadienylchromium dichloride derivative described above was stirred overnight in 20 ml dry tetrahydrofuran under an atmosphere of pure NO. After filtration and drying at 10^{-3} torr and room temperature for two days, a yellowish-green material was obtained; its IR absorptions at 1800 and 1700 cm^{-1} were identical with those of the product obtained from treatment of the tricarbonyl hydride derivative with CHCl_3 and NO.

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