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SYNTHESIS OF SOME NOVEL σ-ALKYL-π-CYCLOPENTADIENYL-TUNGSTEN TRICARBONYL COMPLEXES

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Summary

Six σ-alkyl-π-cyclopentadienyltungsten tricarbonyls, π-$C_5H_5W(CO)_3$-σ-R (R = i-Pr, n-Bu, i-Bu, sec-Bu, n-Am and i-Am) have been synthesised. The IR spectra of these derivatives exhibited two strong C—O stretching bands, one between 2012—2000 and the other between 1931—1922 cm^{-1}. In addition, a well defined shoulder at ~1880 cm^{-1} has also been noted in some cases.

Introduction

From the literature data it is observed that the complexes π-$C_5H_5M(CO)_3$-σ-R show the order [1] of stability M = W ⩽ Mo >> Cr. When R = alkyl, the chromium derivatives are either unknown or are very unstable, whilst the molybdenum complexes are fairly stable. The tungsten alkyls appear to be slightly less stable than the molybdenum analogues and also they are difficult to prepare. The methyl derivative was prepared by the action [2] of diazomethane on π-$C_5H_5W(CO)_3H$. Both methyl [3] and ethyl [3] derivatives have also been prepared by the action of alkyl halides on the sodium salt of cyclopentadienyltungsten tricarbonyl anion. The corresponding isopropyl analogue could not be isolated by this method. It was obtained by protonation [1] and subsequent reduction of the σ-allyl complex, π-$C_5H_5W(CO)_3$-σ-C_3H_5. In this method the propene cation $[\pi\text{-}C_5H_5W(CO)_3(CH_3CH{=}CH_2)]^+$ formed after the protonation of the σ-allyl complex is reduced with sodium borohydride to the σ-isopropyl complex. In our laboratory we have been able to prepare the σ-isopropyl complex directly by the action of isopropyl iodide on $NaC_5H_5W(CO)_3$. Other σ-alkyl complexes which contain n-butyl-, isobutyl-, sec-butyl-, n-amyl- and isoamyl- groups have also been synthesised.

Discussion

The complexes were prepared in 35—64% yield by stirring a mixture of the appropriate alkyl halide and a benzene solution of π-$C_5H_5W(CO)_3Na$ at room

TABLE 1

C—O STRETCHING FREQUENCIES FOR π-$C_5H_5W(CO)_3$-σ-ALKYL COMPLEXES

Complex	ν(CO) (cm^{-1})
(π-C_5H_5)$W(CO)_3$-σ-(iso-C_3H_7)	2007vs, 1925vs
(π-C_5H_5)$W(CO)_3$-σ-(n-C_4H_9)	2012vs, 1923vs, 1880(sh)
(π-C_5H_5)$W(CO)_3$-σ-(iso-C_4H_9)	2000vs, 1923vs
(π-C_5H_5)$W(CO)_3$-σ-(sec-C_4H_9)	2007vs, 1930vs
(π-C_5H_5)$W(CO)_3$-σ-(n-C_5H_{11})	2007vs, 1922vs, 1872(sh)
(π-C_5H_5)$W(CO)_3$-σ-(iso-C_5H_{11})	2011vs, 1931vs, 1889(sh)

temperature under nitrogen for about 5 h. These complexes dissolved in most organic solvents except aliphatic hydrocarbons and alcohols. They were very air-sensitive.

The IR spectra of the complexes exhibited two very strong C—O bands (Table 1), one between 2012—2000 and the other between 1931—1922 cm^{-1}. A well defined shoulder at ~1880 cm^{-1} was also recorded in the IR spectra of the n-butyl-, n-amyl- and isoamyl-derivatives. The appearance of this shoulder band may be attributed to the splitting of E mode into $A' + A''$ modes. All these spectra bear a strong resemblance to the spectra of known molybdenum compounds except a slight shift of frequencies in the lower region.

Experimental

General

π-$C_5H_5W(CO)_3Na$ was prepared by reduction of $[\pi$-$C_5H_5W(CO)_3]_2$ with 1% sodium amalgam in benzene as described in the literature [4]. The alkyl halides were distilled before use. All the reactions and manipulations were performed in a nitrogen atmosphere. The IR spectra were recorded in KBr discs using a P.E. infrared spectrophotometer model 137.

Preparation of σ-isopropyl-(π-cyclopentadienyl)tungsten tricarbonyl

Isopropyl iodide (2.0 ml) was added dropwise to a benzene solution of the sodium salt of cyclopentadienyltungsten tricarbonyl (prepared from 0.2 g $[\pi$-$C_5H_5W(CO)_3]_2$). The reaction mixture was stirred for 5 h with a magnetic stirrer. After this period the reaction mixture became turbid. The solvent was removed in vacuo. The residue so obtained was washed first with a small quantity of water (to remove sodium iodide formed as a result of the reaction) and then with alcohol and diethyl ether. The solid compound was extracted with benzene (10 ml). An insoluble greenish black substance remained undissolved. The IR spectrum of this substance showed no C—O bands. To the benzene solution 10 ml hexane was added. A yellow-brown solid separated from the solution. It was filtered and dried in vacuo. Further crystallisation of this substance gave an intractable decomposition product. The yellow-brown solid was shown to be σ-isopropyl-(π-cyclopentadienyl)tungsten tricarbonyl. Yield 35.3%, m.p. 140° dec. (Found: C, 35.01; H, 3.20; W, 48.96. $C_{11}H_{12}O_3W$ calcd.: C, 35.10; H, 3.19; W, 48.93%.) It was insoluble in water, hexane, petroleum ether, diethyl ether, methanol, ethanol, but dissolved in benzene, toluene, xylene, tetrahydrofuran, acetone, chloroform, carbon tetrachloride etc.

Preparation of σ-n-butyl-(π-cyclopentadienyl)tungsten tricarbonyl

Similarly a mixture of n-butyl iodide (2 ml) and π-$C_5H_5W(CO)_3Na$ (prepared from 0.2 g of the dimer) was stirred for 6 h to give a yellow-orange substance. Yield: 64.0%, m.p. 145°C (dec.) (Found: C, 37.00; H, 3.55; W, 47.19. $C_{12}H_{14}O_3W$ calcd.: C, 36.92; H, 3.59; W, 47.17%).

Preparation of σ-isobutyl-(π-cyclopentadienyl)tungsten tricarbonyl

On stirring a mixture of isobutyl iodide (2 ml) and a benzene solution of π-$C_5H_5(CO)_3Na$ (prepared from 0.2 g of the dimer) for $4\frac{1}{2}$ h, a yellow-brown solid was obtained. Yield 59.7%, m.p. 156°C (dec.) (Found: C, 36.88; H, 3.59; W, 47.20. $C_{12}H_{14}O_3W$ calcd.: C, 36.92; H, 3.59; W, 47.17%).

Preparation of σ-sec-butyl-(π-cyclopentadienyl)tungsten tricarbonyl

A mixture of sec-butyl iodide (2 ml) and a benzene solution of π-$C_5H_5W(CO)_3Na$ (prepared from 0.2 g of the dimer) was stirred at room temperature for 5 h. Work up as for the σ-isobutyl- analogue gave a yellowish brown substance. Yield 42.7%, m.p. 142°C (dec.) (Found: C, 36.95; H, 3.60; W, 47.19. $C_{12}H_{14}O_3W$ calcd.: C, 36.92; H, 3.59; W, 47.17%).

Preparation of σ-n-amyl-(π-cyclopentadienyl)tungsten tricarbonyl

Similarly a mixture of n-amyl iodide (2 ml) and π-$C_5H_5W(CO)_3Na$ (prepared from 0.2 g of the dimer) was stirred for 5 h to give a yellow-brown substance. Yield: 61.8%, m.p. 140°C (dec.) (Found: C, 38.63; H, 3.92; W, 45.55. $C_{13}H_{16}O_3W$ calcd.: C, 38.61; H, 3.96; W, 45.53%).

Preparation of σ-isoamyl-(π-cyclopentadienyl)tungsten tricarbonyl

A mixture of isoamyl iodide (2 ml) and a benzene solution of π-$C_5H_5W(CO)_3Na$ (prepared from 0.2 g of the dimer) was stirred at room temperature for 5 h. Workup as for the σ-n-amyl analogue gave a yellowish brown substance. Yield 57.6%, m.p. 135°C (dec.) (Found: C, 38.59; H, 3.90; W, 45.56. $C_{13}H_{16}O_3W$ calcd.: C, 38.61; H, 3.96; W, 45.53%).

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