

NOTIZEN

Synthesis and NMR Study of (η^6 -1,4-diphenyl-1,3-butadiene)tricarbonylchromium(0)

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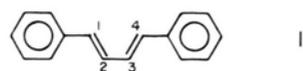
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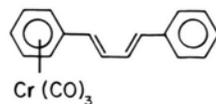
Chromiumcarbonyl, 1,4-Diphenylbutadiene

(η^6 -1,4-Diphenyl-1,3-butadiene)tricarbonylchromium(0) has been synthesized in high yield by using an improved procedure, from tris(acetonitrile)chromium(0) and 1,4-diphenyl-1,3-butadiene. The IR and NMR spectroscopic data show that the organic ligand is bonded to the $\text{Cr}(\text{CO})_3$ moiety through only one of the two phenyl rings.

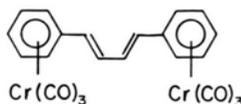
Arenes have been widely used as π -accepting ligand in organometallic chemistry. Particularly, arene complexes of the tricarbonylchromium fragment have found applications as catalyst in the synthesis of organic compounds including several biochemical interest [1] and therefore been studied extensively [2]. Complexes of conjugated diene of the tetracarbonylchromium fragment are also well characterised compounds [3] of potential interest for the catalytic reactions of dienes, like hydrogenation [4]. Complexes of a ligand containing both the aromatic ring and a conjugated diene unit also seem to be interesting for catalytic applications as well as for a structural study. 1,4-Diphenyl-1,3-butadiene (**1**) is one of the representatives for such ligands. **1** has been found to coordinate to the tricarbonyliron(0) moiety through its diene unit [5] and to tricarbonylchromium(0) units through one or both of its phenyl rings [6, 7]. However, both of these early reports on (η^6 -1,4-diphenyl-1,3-butadiene)tricarbonylchromium(0) (**2**) and (η^6 : η^6 -1,4-diphenyl-1,3-butadiene)bis(tricarbonylchromium(0)) (**3**) lack on NMR spectroscopic data which would provide further structural information. This prompted us some years ago to study the coordination properties of **1** towards carbonylmetal frag-



1



2



3

ments of the group 6B elements. Interestingly we found that UV irradiation of **1** in the presence of hexacarbonylmetal(0) yields only tetracarbonyl- (η^4 -1,4-diphenyl-1,3-butadiene)tungsten(0) [8]. The treatment of **1** with 1 or 2 equivalents of tricarbonyltris(acetonitrile)chromium(0) in THF at moderate temperature gave **2** or **3** in high yield, respectively. Both compounds were isolated and studied spectroscopically. Very recently R. D. Rieke and his coworkers published a study on the synthesis and reactivity of **3** which presented similar spectral features [9] as those of a product prepared by us. In this letter we would like to report a facile new synthetic method for **2** and its NMR data.

Experimental

The thermal reactions were performed in a reaction flask with a water cooled refluxer. Anaerobic conditions were assured by Schlenck techniques throughout, using argon as inert gas. Solvents (Merck) were distilled over metallic sodium or phosphorus pentoxide and stored under argon. Characterisation of the products: IR spectra, Perkin Elmer 1430; NMR spectra, Bruker AC 80 spectrometer; the C,H elemental analyses were carried out on a HP 185 CNH analyser. Hexacarbonylchromium(0) was purchased from Ventron and used as received. Tricarbonyltris(acetonitrile)chromium(0) was prepared according to the known procedure [10].

(η^6 -1,4-Diphenyl-1,3-butadiene)tricarbonylchromium(0) (**2**): A solution of 1.0 g (3.9 mmol) tricarbonyltris(acetonitrile)chromium(0) and 0.8 g (3.9

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mmol) 1,4-diphenyl-1,3-butadiene in 50 ml THF is refluxed for two days. After removing the solvent in vacuum the reddish residue is dissolved in dichloromethane and transferred to a chromatography column (silica gel and *n*-hexane). The complex is eluted with a mixture of *n*-hexane and dichloromethane (1:5). Crystallization from *n*-hexane solution yields red crystals (0.9 g, 68%); m.p. 156 °C.

Analysis for $C_{19}H_{14}O_3Cr$

Calcd C 66.6 H 4.09,

Found C 67.4 H 4.12.

Results and Discussion

Refluxing of **1** with tricarbonyltris(acetonitrile)chromium(0) in THF for two days yields **2** which is isolated and purified by column chromatography. The IR spectrum of **2** shows two strong absorption bands in the CO stretching region (1970, 1904 cm^{-1} in *n*-hexane) which is typical for (arene)Cr(CO)₃ complexes.

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **2** gives eight signals for phenyl carbons and four signals for the diene unit of the 1,4-diphenyl-1,3-butadiene ligands as well as one signal for the carbonyl ligands (Table I). This clearly indicates that after coordination the 1,4-diphenyl-1,3-butadiene ligand is not composed of two equal parts any more. Furthermore, four of eight phenyl signals are highly shifted towards higher magnetic field (almost by 30–40 ppm), which parallels the coordination shifts observed for **3**, while the other four do not show any significant change. Since one observes only slight changes in the chemical shifts of the olefinic carbons, it is not unrealistic to suggest a coordination of Cr(CO)₃ moiety to one phenyl group rather than the diene unit. It is noteworthy to mention that the ^{13}C NMR chemical shifts of the coordinated phenyl ring in **2** are very similar to those of **3** while the uncoordinated one has essentially the same chemical shifts as the phenyl groups of **1**. The reason for high shielding of the coordinated phenyl group is the electron flow from the filled metal *d*

Table I. ^{13}C NMR chemical shifts (δ ppm rel. to TMS) in chloroform-*d*.

		1	2	3
Phenyl (coord.)	<i>ipso</i>		106.01	106.91
	<i>ortho</i>		92.76	94.79
	<i>meta</i>		90.70	93.97
	<i>para</i>		91.15	92.29
Phenyl (uncoord.)	<i>ipso</i>	137.57	136.83	
	<i>ortho</i>	129.02	128.82	
	<i>meta</i>	126.44	126.78	
	<i>para</i>	126.82	127.67	
diene	1	129.36	135.40	131.76
	2	132.89	131.75	131.21
	3	132.89	128.82	131.21
	4	129.36	128.29	131.76
CO		233.05	233.45	

orbitals to empty π^* orbitals of the phenyl ring *via* metal→ligand back bonding as observed in other arene complexes of transition metals [11]. The assignment of the four signals to the phenyl carbons is based on the results of a DEPT experiment and the relative signal intensities in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum without NOE. The chemical shifts of the olefinic carbons show a slight decrease on passing from the coordinated side of the ligand to the uncoordinated side. The observation of one ^{13}C NMR signal for the carbonyl groups is attributed to fast CO scrambling found in most of the transition metal arene complexes [12].

The ^1H NMR spectrum of **2** shows two multiplets around 7.3 and 5.4 ppm for the uncoordinated and coordinated phenyl groups, respectively. For the olefinic protons one observes a complex multiplet between 7.0 and 6.0 ppm implying that the ligand is not coordinated through its diene unit. These ^1H NMR observations provide additional compelling evidence for the coordination of the 1,4-diphenyl-1,3-butadiene to the Cr(CO)₃ moiety through one of the phenyl rings.

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