Synthesis and Stereochemical Study of Tetracarbonyl(η^4-1,4-diphenyl-1,3-butadiene)tungsten(0)

SAİM ÖZKAR and N. BEKİR PEYNİRCİOĞLU

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

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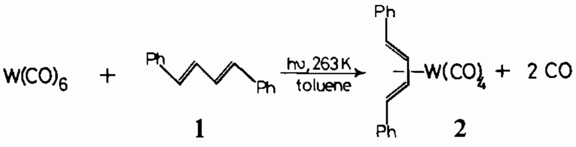
Abstract

trans,trans-1,4-Diphenyl-1,3-butadiene reacts photochemically with hexacarbonyltungsten (0) to form the complex tetracarbonyl(η^4-1,4-diphenyl-1,3-butadiene)tungsten(0). A pseudooctahedral structure is observed spectroscopically. Attempts to form similar complexes with chromium and molybdenum failed.

Introduction

Conjugated dienes are known to form tetracarbonyl(η^4-diene)metal(0) complexes only with chromium [1]. Analogous complexes with molybdenum and tungsten have not yet been prepared. Isolated dienes such as bicyclo[2.2.1]hepta-2,5-diene and 1,5-cyclooctadiene, however, were found to form complexes of the same type with all elements of 6B group [2, 3]. In this study, a novel example of a complex formation between a conjugated diene, *trans,trans*-1,4-diphenyl-1,3-butadiene (**1**), and tungsten is presented. Hexacarbonyltungsten(0) reacts photochemically with **1** in toluene at 263 K to form tetracarbonyl(η^4-1,4-diphenyl-1,3-butadiene)tungsten(0) (**2**). The product **2** was purified by column chromatography and crystallization before the spectroscopic studies. Hexacarbonylchromium(0) and -molybdenum(0) failed to give any reaction with **1** under the same reaction conditions.



Experimental

All reactions and purifications were performed under a prepurified nitrogen atmosphere. Solvents were distilled from sodium or phosphorus pentoxide. *trans,trans*-1,4-diphenyl-1,3-butadiene (**1**) was prepared by condensation of cinnamaldehyde and phenylacetic acid [4]. IR spectra were recorded in toluene on a Perkin-Elmer 1430 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 and Varian CFT 20 spectrometers.

Tetracarbonyl(η^4-1,4-diphenyl-1,3-butadiene)tungsten(0)

A solution of hexacarbonyltungsten(0) (400 mg, 1.14 mmol) and 1,4-diphenyl-1,3-butadiene (250 mg, 1.21 mmol) in toluene (70 ml) was irradiated at 263 K for eight hours, using a mercury UV lamp (TQ 150, Quarzlampen Gmbh, Hanau, F.R.G.). After filtration of the solution, the solvent was removed in vacuum, leaving a brown residue which was taken up in toluene and transferred to a chromatography column packed with silicagel and n-pentane. Elution of the column with a mixture of toluene: n-pentane (1:10) gave a reddish brown band. Upon evaporation of the reddish brown eluate the residue was dissolved in n-pentane (20 ml). When cooled, the solution yielded reddish brown crystals, which were dried under vacuum to yield 270 mg (47%) of $W(CO)_4(C_{16}H_{14})$. *Anal.* Found: C, 48.0; H, 2.85, Calc. for $C_{20}H_{14}O_4W$: C, 47.8; H, 2.81%.

Results and Discussion

The IR spectrum of the tetracarbonyl(η^4-1,4-diphenyl-1,3-butadiene)tungsten(0) complex (**2**) shows four strong absorption bands of about equal intensities for CO stretching at 2030, 1972, 1946, and 1932 cm^{-1}. This indicates a C_{2v} symmetry for the $M(CO)_4$ part of the pseudooctahedral molecule, having four IR-active CO stretching modes of pattern $2A_1 + B_1 + B_2$ [5]. The CO force constants were calculated from the CO stretching frequencies by using the Cotton–Kraihanzel method [6] and found to be 1610 N m^{-1} for the CO groups *trans* to each other and 1522 N m^{-1} for CO groups *trans* to a C=C bond of the olefin ligand.

The ^{1}H NMR spectrum of the complex consists of two multiplets at δ 5.85 and 3.56 ppm for the

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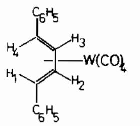
olefinic protons and a complex multiplet centred at 7.26 ppm for the aromatic protons. The signals for the olefinic protons appear as AA′BB′ system. The protons at C1 and C4 (H1 and H4) are A and A′; the ones at C2 and C3 (H2 and H3) are B and B′. The same pattern is observed for **1**. The AA′ part of the spectrum is shown in Fig. 1 for **1** and **2**. The analysis of the spectra reveals ^1H NMR chemical shifts and coupling constants, which are listed in Table I. The resonance frequencies of the olefinic protons shift appreciably towards higher magnetic field upon coordination. The coordination shifts of H1, H4 and H2, H3 are 3.11 and 1.17 ppm, respectively. The large coordination shift observed for H_1, H_4 is attributed to preservation of the *trans,trans* geometry of diene **1** in the complex. This is also evidenced by the large coupling constant (J(H1–H2) = 11.7 Hz).

TABLE I. ^1H NMR Chemical Shifts (δ in ppm, relative to TMS) and $J(^1H-^1H)$ Coupling Constants (Hz) of Free and Coordinated 1,4-Diphenyl-1,3-butadiene in Dichloromethane-d_2 at 293 K

	Free **1**	Coordinated **2**	
δ H1, H4	6.67	3.56	
δ H2, H3	7.02	5.85	
δ C_6H_5	7.30	7.26	
^3J(H1–H2)	15.5	11.7	
^4J(H1–H3)	−0.7	−1.9	
^5J(H1–H4)	0.0	0.0	
^3J(H2–H3)	10.2	4.5	

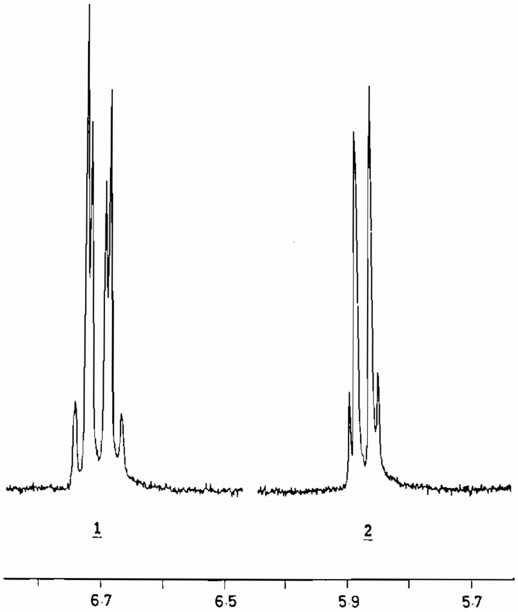


Fig. 1. AA parts of the ^1H NMR spectra of 1 and **2**.

TABLE II. ^{13}C NMR Chemical Shifts (δ in ppm relative to TMS) of 1 and **2** in Dichloromethane-d_2 at 233 K

	1	**2**
C1, C4	128.78	72.32
C2, C3	132.47	78.67
Aromatics	137.30	136.78
	128.52	128.57
	127.41	127.54
	126.21	126.15
CO		210.93(2)[a]
		203.26(1)
		202.09(1)

[a] Relative peak intensity.

The $^{13}C\{^1H\}$ NMR spectra of the diene **1** and the complex **2** were taken in dichloromethane-d_2 and show two peaks for olefinic and four for aromatic carbons. The spectrum of **2** gives three additional signals of relative intensities 2:1:1 for the carbonyl groups (Table II), which excludes any structure with *s-trans* conformation of the diene. An *s-trans* conformation would cause two CO signals of equal intensity to appear. Large coordination shifts are observed for the olefinic carbons as expected [7]. The assignment of the olefinic signals is based on their relative chemical shifts. An exact assignment of the aromatic signals has not been possible, except that the signal of the substituted aromatic carbon could be distinguished at δ 137.30 (**1**) and 136.78 ppm (**2**) by using edited ^{13}C NMR techniques (DEPT).

The ^1H and ^{13}C NMR spectra do not show any significant temperature dependence in the observed range of 203–303 K, indicating the absence of any NMR observable ligand mobility.

Conclusion

The IR and NMR spectral data indicate that the complex **2** exists in a pseudooctahedral structure, in which the diene occupied two *cis* coordination sites. Moreover, the diene retains its *trans,trans* configuration in **2**. In accordance with our earlier observations [1] the diene ligand is found to exist in *s-cis* conformation.

In contrast to the results of the previous studies involving conjugated dienes and the elements of the 6B group, where the formation of tetracarbonyl–diene–metal(0) complexes is observed with chromium(0) and not with tungsten [1, 8] the *trans,trans*-1,4-diphenyl-1,3-butadiene (**1**) is found to form such a complex only with tungsten.

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