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Synthesis and Spectroscopic Study of Tricarbonyltrimethylphosphite-(η^4-cyclooctatetraene)tungsten(0)

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Abstract

Pentacarbonyltrimethylphosphitetungsten(0) reacts photochemically with cyclooctatetraene to give a tricarbonyltrimethylphosphite(η^4-cyclooctatetraene)tungsten(0) complex, which exists in both facial and meridional isomeric forms.

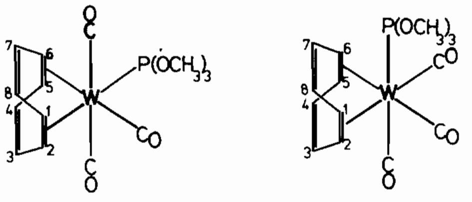
Introduction

Cyclooctatetraene, COT, can bond to transition metals in an unparalleled variety of ways. It may act as a mono-olefin, as a 1,3- or 1,5-diene, as a 1,3,5-triene or as a tetraene system. In addition, examples of σ-bonding and π-allyl bonding are known in COT-metal compounds. In its complexes with the group 6B metals, COT adopts preferentially 1,3,5-triene (hexahapto) systems. So it forms the $M(CO)_3$-(η^6-COT) complexes with chromium, molybdenum and tungsten [1–3]. The one exception of this general behavior was the $Mo(CO)_4$(η^4-COT) complex which has been synthesized from $Mo(CO)_3$-(η^6-COT) by CO insertion [4]. We have recently reported the synthesis of the stable tungsten analogue, $W(CO)_4$(η^4-COT), by UV irradiation of hexacarbonyltungsten(0) in the presence of COT at low temperature [5].

The presence of a bulky donor ligand such as trimethylphosphite in the complex would be expected to affect the coordination ability of the COT ligand. In order to investigate this effect in the case of the group 6B metals, we studied the reaction of $M(CO)_5[P(OCH_3)_3]$ (M: Cr, Mo, W) with COT. Since the UV irradiation of $M(CO)_5$-(PR_3) in the presence of olefin proved a convenient means of synthesizing carbonyl–donor ligand–olefin–metal complexes [6], the pentacarbonyltrimethylphosphitemetal(0) was irradiated in the presence of COT in an inert solvent. Only the tricarbonyltrimethylphosphite(η^4-COT)tungsten(0) complex was isolated as a product of the photochemical reaction:

$$W(CO)_5[P(OCH_3)_3] + COT \xrightarrow[\text{n-pentane}]{h\nu,\ 253\ K} W(CO)_3[P(OCH_3)_3](\eta^4\text{-COT}) + 2CO$$

The complex has a pseudooctahedral structure and exists in two isomeric forms depending upon the relative position of the trimethylphosphite ligand with respect to the COT ligand (Fig. 1).



mer *fac*

Fig. 1. The two possible isomers of the tricarbonyltrimethylphosphite(η^4-cyclooctatetraene)tungsten(0) complex.

Experimental

All reactions and purifications were performed under a prepurified nitrogen atmosphere. Solvents were distilled from sodium or phosphorus pentoxide. The pentacarbonyltrimethylphosphitetungsten(0) was prepared according to the published procedure [7].

IR-spectra were recorded on a Perkin-Elmer 297 spectrophotometer. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WP 200 spectrometer operating in the FT mode.

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Tricarbonyltrimethylphosphite(η^4-cyclooctatetraene)tungsten(0)

A solution of 300 mg pentacarbonyltrimethylphosphitetungsten(0) and 1 cm^3 cyclooctatetraene in 100 cm^3 n-pentane was irradiated at 253 K for three hours using a mercury UV lamp (TQ 150, Quarzlampen GmbH, Hanau/B.R.D.). After the filtration of the solution, the solvent and the excess cyclooctatetraene were removed by evaporation in vacuum, leaving a yellow residue which was redissolved in dichloromethane and transferred to a chromatography column filled with silicagel and n-pentane. Eluting the column with a mixture of dichloromethane:n-pentane (1:5) gave a yellow band. The yellow eluate was evaporated in vacuum. The residue was dissolved in 10 cm^3 n-pentane. Upon cooling, the solution yielded yellow crystals which were dried in vacuum to yield 240 mg or 80% of $W(CO)_3[P(OCH_3)_3](C_8H_8)$ (Found: C, 33.8%; H, 3.45%. $C_{14}H_{17}O_6PW$ requires C, 33.9%; H, 3.46%).

Results and Discussion

The IR-spectrum of the tricarbonyltrimethylphosphite(η^4-cyclooctatetraene)tungsten(0) complex shows five absorption bands for the CO stretchings (Fig. 2), indicating that the complex exists in both *mer-* and *fac*-isomeric forms. Since one of the five peaks has comparatively high intensity, an absorption band of the *fac*-isomer apparently overlaps with one of the three absorption bands of the *mer*-isomer. The assignment of absorption bands to the isomers is based on the intensity distribution and the relative positions of the bands [8]. The CO force constants were calculated from the carbonyl stretching frequencies using the Cotton–Kraihanzel approximation [9]. The CO stretching frequencies and CO force constants are listed in Table I. The average $\bar{k}$ values are lower than that of the tetracarbonyl(η^4-COT)tungsten(0) complex [5], indicating the effect of the trimethylphosphite ligand on bonding in the complex.

TABLE I. The CO Stretching Frequencies and the CO Force Constants of *mer-* and *fac*-$W(CO)_3[P(OCH_3)_3](\eta^4$-COT). k_1 refers in *fac-* and *mer*-isomers to the CO ligand which is *trans* to trimethylphosphite or to a double bond of COT respectively. k_2 refers to the remaining CO groups. $\bar{k}$ is the average of k_1 and k_2.

	ν_{CO} (cm^{-1})			CO Force constants (Nm^{-1})		
	A'(1)	A'(2)	A''	k_1	k_2	$\bar{k}$
mer-	1930	1877	1883	1444	1457	1450
fac-	1977	1945	1877	1400	1564	1482

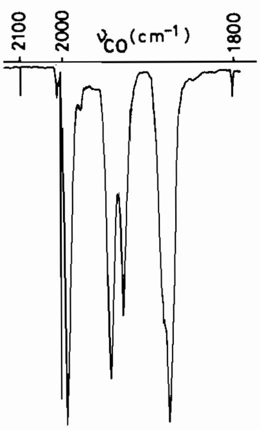

Fig. 2. The IR spectrum of $W(CO)_3[P(OCH_3)_3](\eta^4$-COT) in the region of CO stretchings recorded from n-pentane solution.

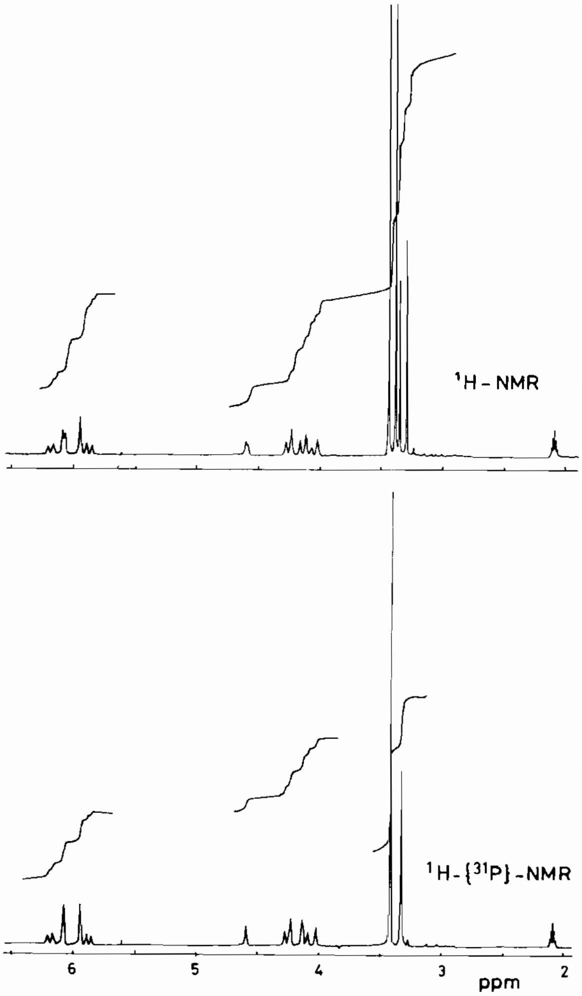

Fig. 3. The ^{1}H NMR and ^{1}H–{^{31}P} NMR spectra of the tricarbonyltrimethylphosphite(η^4-cyclooctatetraene)tungsten (0) complex in toluene-d_8 at room temperature.

The ^1H NMR spectrum of the complex consists of 10 signals which are split due to the proton–phosphorus as well as proton–proton coupling. For simplification of the complicated ^1H NMR spectrum a heteronuclear decoupling experiment was undertaken [10]. Both the ^1H NMR and $^1H-\{^{31}P\}$ NMR spectra of the complex are given in Fig. 3. and on a larger scale in Fig. 4. The signals are distinguished into two groups based on their relative intensities and structures, each corresponding to one of the two isomers of the complex. Because of the π-competition, the protons of the trimethylphosphite ligand in the *fac*-form are expected to resonate at a lower magnetic field than those in the *mer*-form. Therefore the higher chemical shift for the trimethylphosphite is assigned to the *fac*-isomer. The signals of the olefinic protons were assigned by considering the spin systems in both isomers. From the relative intensities of the trimethylphosphite signals of *mer*- and *fac*-isomers, the equilibrium composition of the solution was found to be 33% *mer*- and 67% *fac*-isomer. The assignment of signals to the olefinic protons is based on their chemical shifts and fine structures. The ^1H NMR chemical shifts and the coupling constants are given in Table II.

The $^{13}C-\{^1H\}$ NMR spectrum of the complex was recorded from its toluene-d_8 solution and is given in Fig. 5. For the carbon atoms of the COT ligand two signal groups are distinguishable, each consisting of four signals. The four signals between 132–137 ppm are to be assigned to the uncoordinated carbon atoms and the other four signals between 79–96 ppm to the coordinated carbon atoms of the COT ligand. In each group, the signals of lower intensities are assigned to the *mer*-isomer and the other ones to the *fac*-isomer. Furthermore, the consideration of the doublet structure of some signals and the chemical shift values enables us to make the complete assignment of the signals to the individual carbon atoms of the COT ligand in both isomers.

For the carbon atoms of the trimethylphosphite ligand, the $^{13}C-\{^1H\}$ NMR spectrum shows two doublets at 51.75 and 52.06 ppm due to the $^{13}C-^{31}P$ coupling. The doublet of lower intensity at higher magnetic field is readily assigned to the *mer*-isomer, which has the trimethylphosphite ligand in a position *trans* to a double bond having less π-accepting ability than carbon monoxide. In the carbonyl region of the ^{13}C-NMR spectrum, four doublets are observed due to the $^{13}C-^{31}P$ coupling. The assignment of the signals to carbonyl groups in both isomers is based on the chemical shift values and the relative intensities of the signals. The ^{13}C NMR chemical shift and $^{13}C-^{31}P$ coupling constant values are given in Table III. The resonance frequencies of the carbon atoms are shifted to higher magnetic field on coordination as expected [11].

The $^{31}P-\{^1H\}$ NMR spectrum of the complex was also recorded from its toluene-d_8 solution by using H_3PO_4 as external reference. It shows two singlets at 148.22 and 139.84 ppm with their tung-

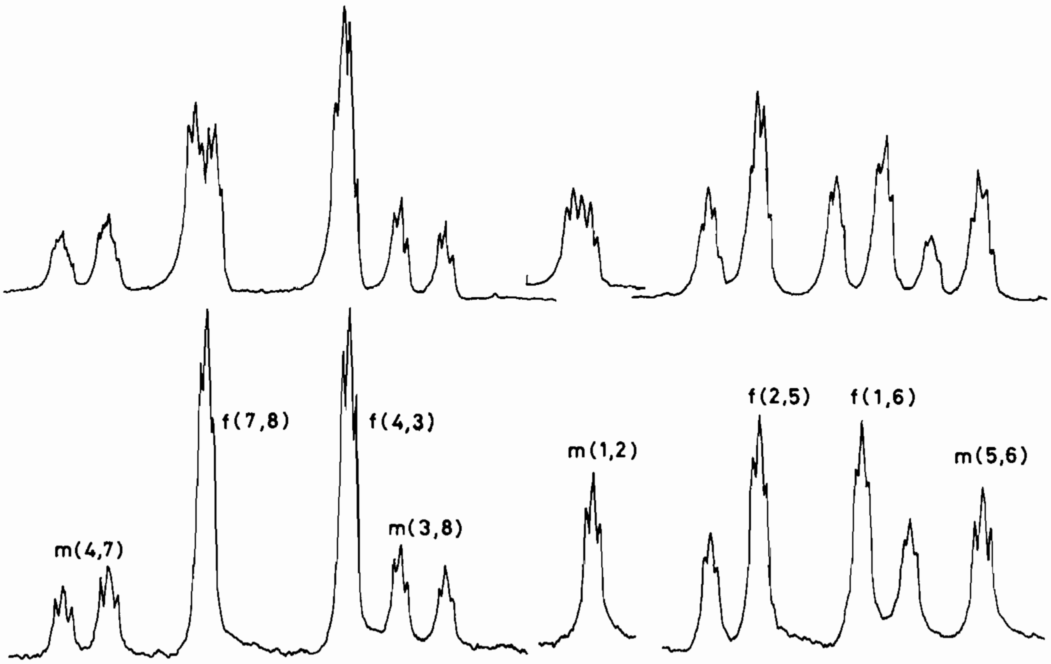

Fig. 4. The ^1H NMR (above) and $^1H-\{^{31}P\}$ NMR (below) spectra of the complex on a larger scale.

TABLE II. ^1H NMR Chemical Shifts (in ppm, relative to TMS as internal reference), $J_{^{31}P-^1H}$ and $J_{^1H-^1H}$ Coupling Constants (Hz) of *mer*- and *fac*-$W(CO)_3[P(OCH_3)_3](\eta^4$-COT) in Toluene-$d_8$ at Room Temperature.

	δ (ppm)	$J_{^{31}P-^1H}$ (Hz)	$J_{^1H-^1H}$ (Hz)
$H_{1,6}$	4.12	9.5	$H_1-H_2=H_5-H_6=9.1$
$H_{2,5}$	4.25	1.0	$H_1-H_8=H_6-H_7=1.8$
fac- $H_{3,4}$	5.95	1.3	$H_1-H_3=H_4-H_6=1.6$
$H_{7,8}$	6.09	4.0	$H_2-H_3=H_4-H_5=1.4$
$P(OCH_3)_3$	3.42	10.8	$H_2-H_8=H_5-H_8=1.3$
$H_{1,2}$	4.60	3.5	$H_2-H_3=H_1-H_8=1.4$
$H_{3,8}$	5.87	–	$H_2-H_8=H_1-H_3=1.2$
mer- $H_{4,7}$	6.19	0.8	$H_3-H_4=H_7-H_8=8.3$
$H_{5,6}$	4.02	0.8	$H_4-H_5=H_6-H_7=2.0$
$P(OCH_3)_3$	3.33	11.4	$H_4-H_6=H_5-H_7=1.4$

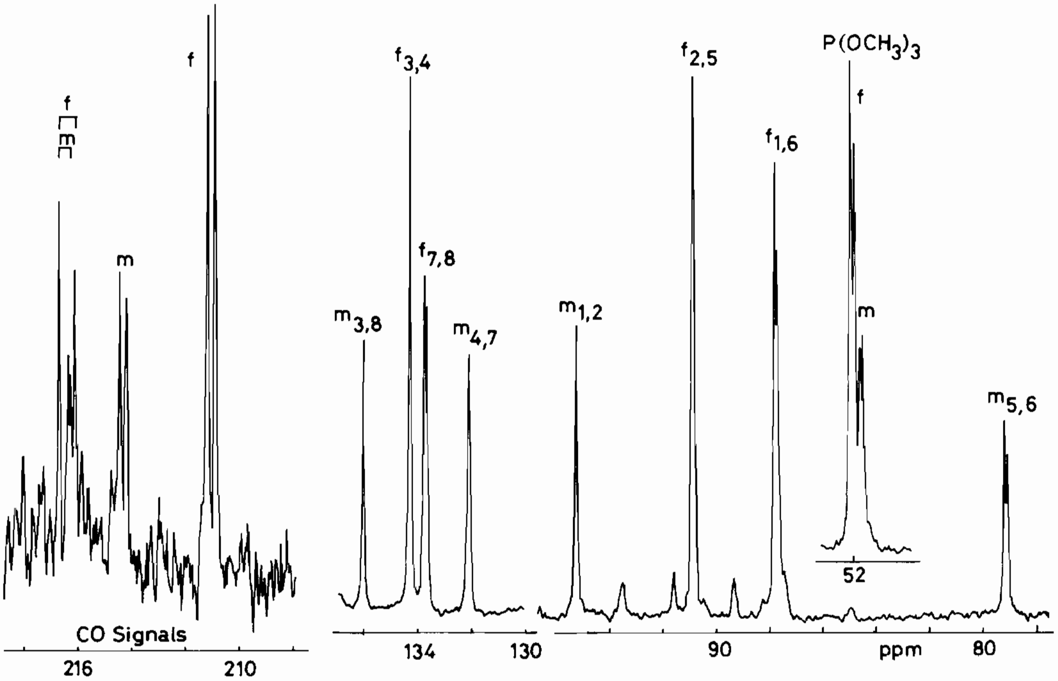

Fig. 5. The $^{13}C-\{^1H\}$ NMR spectrum of $W(CO)_3[P(OCH_3)_3](\eta^4$-COT) in toluene-$d_8$ at room temperature.

sten satellites with $J_{^{183}W-^{31}P}$ values of 491 and 346 Hz for the *mer*- and *fac*-isomers respectively. The assignment of signals to the isomers is based on the relative signal intensities. The comparison of the relative intensities of the $^{31}P-\{^1H\}$ NMR signals confirms the equilibrium composition of 67% *fac*- and 33% *mer*-isomers calculated from the ^1H NMR signal intensities. The ^{31}P NMR chemical shift of trimethylphosphite is shifted toward lower magnetic field upon coordination as observed in a large number of phosphine and phosphite complexes [12, 13].

Conclusion

The IR and NMR spectral data indicate that the $W(CO)_3[P(OCH_3)_3](\eta^4$-COT) complex exists both in *fac*- and *mer*-isomers. Since the NMR spectra of the complex do not show any significant change with the temperature between 173–353 K, both isomers are said to be rigid, which is a property of the complexes with unconjugated diene ligands [14]. The presence of a donor ligand such as trimethylphosphite in the complex affects the coordination

TABLE III. The ^{13}C NMR Chemical Shifts (in ppm, relative to TMS as internal reference) and the $^{13}C-^{31}P$ Coupling Constants (Hz) (given in parentheses) of the Complex in Toluene-d_8 at Room Temperature.

	fac-isomer	*mer*-isomer
δC_1	87.78 (3.7)	95.25
δC_2	90.87	95.25
δC_3	134.38	136.11
δC_4	134.38	132.17
δC_5	90.87	79.14 (5.5)
δC_6	87.78 (3.7)	79.14 (5.5)
δC_7	133.80 (3.8)	132.17
δC_8	133.80 (3.8)	136.11
$\delta P(OCH_3)_3$	52.06 (6.3)	51.75 (5.2)
δCO	216.42(29.7)	216.54(17.6)
	211.05(14.3)	214.34(13.3)

ability of the COT ligand. Although the cyclooctatetraene prefers to act as a tridentate ligand toward group 6B metals, the presence of a donor ligand forces it to function only as a bidentate ligand through the carbon atoms 1,2 and 5,6 with tungsten. However, the same conclusion can not be extended to the analogous chromium(0) and molybdenum(0) complexes because the irradiation of $Cr(CO)_5[P(OCH_3)_3]$ and $Mo(CO)_5[P(OCH_3)_3]$ complexes did not give any reaction with COT.

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