

82. (Butadiene)tricarbonylosmium¹⁾ Synthesis and Structural Comparison with the Fe- and Ru-Complexes Based on ¹H- and ¹³C-NMR. Spectroscopy

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Summary

The photochemical synthesis of the title complex from 1,3-butadiene and dodecacarbonyltriosmium is described. The ¹H-NMR. and H-coupled ¹³C-NMR. spectra are analyzed completely and the H,H- and C,H-coupling constants compared with the data of the corresponding Fe- and Ru-complexes. One-bond ¹³C, ¹³C-coupling constants are reported for a series of complexed 1,3-dienes. All data are consistent with an increasing distortion from planarity of the C,H-skeleton at the terminal diene C-atoms in the sequence Fe → Ru → Os.

We have previously shown that nuclear spin coupling constants obtained from the complete analysis of high-resolution H-coupled ¹³C-spectra of transition metal complexed 1,3-dienes yield detailed stereochemical information about the complexed ligand. The results on the parent compounds (1,3-butadiene)tricarbonyliron (1) [2] and (1,3-butadiene)tricarbonylruthenium (2) [3] have indicated that in solution these complexes exhibit a nonplanar ligand skeleton with equalized C,C-bond lengths and considerable rehybridization towards sp³ of the terminal C-atoms. The nonplanar conformation of the diene ligands agrees with a structural model from X-ray data of substituted (butadiene)tricarbonyliron complexes [4]. In order to follow the observed structural trends throughout the iron, ruthenium and osmium group it was necessary to prepare the hitherto unknown (1,3-butadiene)-tricarbonylosmium complex (3).

Thermal reaction of Os₃(CO)₁₂ with 1,3-dienes gives rise to the formation of trinuclear cluster complexes [5] or produces only small yields of mononuclear compounds [6]. A successful photochemical reaction to form mononuclear tricarbonylosmium complexes has been reported in the cases of 1,3-cyclooctadiene [5] and 1,3-cyclohexadiene [7]. Consequently, we have treated 1,3-butadiene with Os₃(CO)₁₂ under photochemical conditions. To speed up the reaction reported to be very slow with cyclohexadiene [7], the photolysis was carried out at 80° which increases the solubility of the metal carbonyl reagent. (1,3-Butadiene)tricarbonyl-

¹⁾ ¹³C-NMR. Spectroscopy, Part XXVI, Part XXV [1].

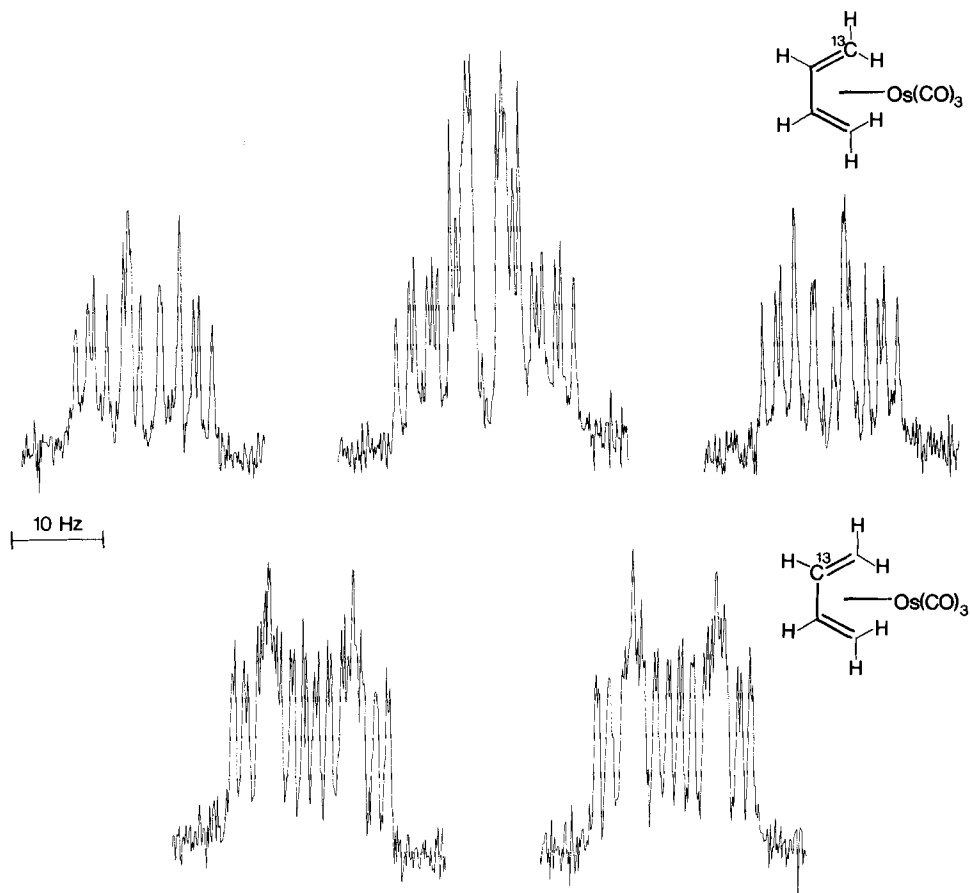
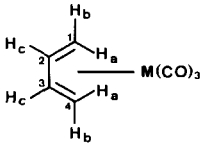


Figure. ^1H -Coupled ^{13}C -NMR. spectrum of (1,3-butadiene)tricarbonylosmium (**3**) (C_6D_6)

osmium (**3**) was isolated as a colourless solid, m.p. 22° , in 55% yield. The analytical characterization is described in the experimental part. (1,3-Pentadiene)tricarbonylosmium (**6**) was obtained in the same way.

The H-NMR. spectrum of **3** was analyzed as an $AA'MM'XX'$ system as described for the Fe- and Ru-complexes [2] [3]. Iterative computer simulation (LAOCOON-3) on 152 experimental line frequencies then gave the set of chemical shifts and H,H-coupling constants listed in *Tables 1* and *2*. The H-coupled ^{13}C -NMR. spectra of the C(1) and C(2) isotopomers are illustrated in the *Figure*. Although the complex is not very stable in solution at room temperature, and despite the extremely long acquisition period of 45 h highly resolved spectra could be obtained which in the case of C(2) display 61 of the calculated 64 transitions with intensity greater than 0.04. A coupling constant of 0.3 Hz is well resolved under these conditions. Also the analysis of the seven-spin systems of such ^{13}C -isotopomers we have previously discussed [2] [3]. Relative signs of coupling constants which turned out to be critical in the course of the analysis, *i.e.*, $^2J(1a, 1b)$,

Table 1. ^1H - and ^{13}C -Chemical shifts (δ [ppm], C_6D_6) of the complexes **1**, **2** and **3**

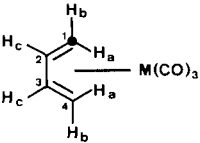
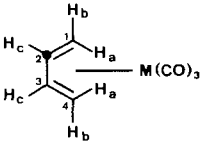
	M =	Fe 1	Ru 2	Os 3
	$\text{H}_a\text{-C}(1,4)$	-0.03	0.12	0.14
	$\text{H}_b\text{-C}(1,4)$	1.46	1.44	1.70
	$\text{H}_c\text{-C}(2,3)$	4.89	4.88	4.93
	$\text{C}(1,4)$	40.53	32.74	24.19
	$\text{C}(2,3)$	85.49	86.31	82.32
	$\text{M}(\text{CO})_3$	212.1	198 ^a)	173 ^a)

^a) Broad due to relatively slow carbonyl exchange.

 Table 2. H, H -Coupling constants J [Hz] of complexes **1**, **2** and **3**²)

	M =	Fe 1	Ru 2	Os 3
$J(\text{H}, \text{H})$	1a, 1b	-2.42	-2.77	-3.48
	1a, 2c	9.33	8.65	7.78
	1b, 2c	6.93	6.94	6.86
	2c, 3c	4.70	4.60	4.32
	1a, 3c	-1.11	-1.10	-1.09
	1b, 3c	1.14	1.10	1.17
	1a, 4a	-0.31	-0.30	-0.37
	1a, 4b	-0.09	-0.13	-0.18
	1b, 4b	0.05	0.02	0.02

 Table 3. C, H -Coupling constants J [Hz] of complexes **1**, **2** and **3**²)

	M =	Fe 1	Ru 2	Os 3	
	$J(\text{C}, \text{H})$	1, 1a	161.52	159.62	159.61
		1, 1b	157.97	156.17	155.12
		1, 2c	3.39	3.64	3.51
		1, 3c	7.75	7.66	7.80
		1, 4a	0.37	0.69	1.42
		1, 4b	1.71	1.64	2.04
	$J(\text{C}, \text{H})$	2, 2c	169.12	168.16	169.74
		2, 1a	-0.02	-0.02	-0.34
		2, 1b	-0.90	-0.82	-1.35
		2, 3c	2.30	2.67	2.98
		2, 4a	4.12	3.93	3.60
		2, 4b	9.37	8.94	9.02

2) For the designation of H, H -, C, H - and C, C -coupling constants the following simplified notation is used: $J(1a, 1b) = J(\text{H}_a\text{-C}(1), \text{H}_b\text{-C}(1))$; $J(2, 3c) = J(\text{C}(2), \text{H-C}(3))$; $J(2, 3) = J(\text{C}(2), \text{C}(3))$ and similarly for other coupling constants.

$^5J(1a, 4a)$ and $^2J(2, 3c)$, $^2J(2, 1b)$ respectively, were assumed to be the same as in the Fe-complex **1** [2]. C-chemical shifts and C,H-coupling constants are listed in *Tables 1* and *3*.

Further structural information about the complexed diene ligand is available from one-bond ^{13}C , ^{13}C -coupling constants ($^1J(C, C)$) which, in principle, can be obtained from the H-decoupled ^{13}C -NMR. spectrum. Preliminary data on tricarbonyliron complexed dienes have indicated [2] that this coupling parameter is sensitive to bond length alternation. Since the parameter has to be determined from isotopomers which contain at least two ^{13}C -nuclei a measurement at natural isotope abundance requires highly purified and reasonably stable substrates, concentrated solutions, and excellent sensitivity and stability of the spectrometer. From symmetrical 1,3-diene ligands only $^1J(1, 2)$ can be obtained, whereas the pentadiene complexes **4**, **5** and **6** yield the data about all three complexed C,C-bonds. Pertinent results on some Fe-, Ru- and Os-tricarbonyl complexes are summarized in *Table 5*.

The structural changes in the complexed ligand as a function of the nature of the transition metal are most clearly reflected in the H,H-, C,H- and C,C-coupling constants. For example in **1**, **2** and **3**, the *geminal* H,H-coupling $^2J(1a, 1b)$ shows a steady trend towards more negative values, which have to be compared with the value of +1.74 Hz in uncomplexed butadiene [8]. This effect was previously ascribed [2] to a significant rehybridization towards sp^3 at the terminal C-atoms C(1,4), in agreement with the geometry of the C,H-skeleton as obtained from X-ray analysis of substituted (butadiene)tricarbonyliron complexes [4]. For comparison, the corresponding values in ethylene (+2.5 Hz) [9], cyclopropane (-4.3) [10] and methane (-12.4) [11] may be consulted. The *vicinal* H,H- and C,H-coupling constants across the terminal C,C-bond show a selective decrease in the case of $^3J'(1a, 2c)$ and $^3J^c(2, 4a)$ ($=^3J^c(3, 1a)$), whereas the corresponding $^3J^c(1b, 2c)$ and $^3J'(2, 4b)$ ($=^3J'(3, 1b)$) are very little affected. Also, the *vicinal* H,H-coupling across the central C,C-bond ($^3J(2c, 3c)$) exhibits only minor changes. If one considers the ratios of the *vicinal trans* and *cis* H,H- and C,H-coupling constants (*Table 4*), it is evident that the observed effects cannot be explained simply by conformational changes about the C(1),C(2)-bond. The influence of the torsional angle φ on the J'/J^c ratio was shown to be very small [2]. The selective decrease of $^3J'(1a, 2c)$ and $^3J^c(2, 4a)$ has previously been attributed to a significant rehybridization at the terminal C-atoms in the Fe- and Ru-complexes [2]. This deviation from planarity for the structural fragment C(2)-C(1), H_a , H_b appears to be even more pronounced in the case of the osmium complex **3**. It is noteworthy that H,H- and C,H-coupling constants involving H_a -C(1) and H_a -C(4) show larger changes than those involving the corresponding H_b -atoms.

Table 4. Ratios of the *vicinal trans* and *cis* coupling constants

	M= Fe 1	Ru 2	Os 3
$^3J'(1a, 2c)/^3J^c(1b, 2c)$	1.35	1.25	1.13
$^3J'(2, 4b)/^3J^c(2, 4a)$	2.27	2.28	2.51

We conclude that $H_c-C(2)$, $C(2)$, $C(1)$ and $H_b-C(1)$ remain more or less in the same relative orientation in the three complexes, whereas H_a is pushed away from the metal atom and below the plane of the other atoms to an increasing extent in the sequence $Fe \rightarrow Ru \rightarrow Os$. This conclusion is supported by the relatively large negative $^2J(H, H)$ -coupling constant (-3.48 Hz) in the osmium complex **3**.

Further information about the bonding situation in transition metal complexed olefins may be obtained from one-bond C, C-coupling constants. This parameter is known to depend upon the *s*-character of the C-orbitals involved in the C, C-bond [12]. To date, very few experimental data have been published, e.g., on methyl-substituted ferrocene [13], (cyclobutadiene)tricarbonyliron [13] and (butadiene)tricarbonyliron [2]. The new data summarized in Table 5 illustrate the following trends. Firstly, $^1J(C, C)$ decreases upon complexation of the diene whereby the values for the C(1), C(2)- and C(2), C(3)-bonds approach the same value within experimental error. Secondly, there is a relatively small dependence on the nature of the transition metal if Ru- and Fe-complexes are compared, whereas in the tricarbonylosmium complexes **3** and **6** $^1J(1, 2)$ decreases by 4–5 Hz when compared with complexes **1**, **2**, **4** and **5**. From X-ray crystal analysis of Fe- [14] and Ru-complexes [15] of this type it is well known that there is very little, if any, bond length alternation in the diene ligand. Although an X-ray analysis of a mononuclear osmium complex has not yet been performed, some information can be obtained from the crystal structures of the clusters (*s-cis*-butadiene) $Os_3(CO)_{10}$ and (*s-trans*-butadiene) $Os_3(CO)_{10}$ [16]. All the available information seems to indicate that C, C- and C, M-bond lengths are not significantly affected if the metal changes in the sequence Fe, Ru, Os. The decrease in the C, C-coupling constants in going from Fe to Os is significant and promises to supply information about the electronic structure of the complexed ligand which is not available from X-ray data. From the three pentadiene complexes together with the data of the butadiene complexes typical values for complexed C, C-bonds can be extracted as follows: 43.5 ± 0.5 Hz for Fe-complexes, 42.3 ± 0.5 Hz for Ru-complexes, and 39 ± 1 Hz for Os-complexes. 1,3-Pentadiene complexes exhibit a significant increase in $J(3, 4)$ due to the influence of the methyl group [13].

Table 5. C, C-Coupling constants J [± 0.3 Hz] of complexed 1,3-dienes

		M =			
		Fe	Ru	Os	Ligand
		1	2	3	
	$J(1, 2)$	43.9	42.4	38.8	68.8 [8]
	$J(2, 3)$	-	-	-	53.7
		4	5	6^a	
	$J(1, 2)$	43.3	42.1	38.0	
	$J(2, 3)$	43.5	42.5	40.2	
	$J(3, 4)$	46.2	44.4	42.5	
	$J(4, 5)$	43.0	41.5	40.5	
		7	8		
	$J(1, 2)$	42.7	40.8		
	$J(1, 6)$	38.5	37.5		

^a) Coupling constants: ± 0.5 Hz.

An interpretation of coordination shifts in transition metal complexes is difficult in terms of structure and bonding. In the present series, there are only small changes in the chemical shift of C(2) in going from the Fe-complex **1** to the Os-complex **3** (Table 1). For the terminal C-atom, however, the shielding increases steadily, **1**: 40.53 ppm, **2**: 32.74 ppm, **3**: 24.19 ppm. This trend is also observed in the pentadiene complexes **4**, **5**, **6** (cf. exper. part) and is consistent with increasing rehybridization towards sp^3 at the terminal C-atoms. The H-shifts of the three butadiene complexes do not exhibit any significant effects.

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Experimental Part

Preparation and handling of all complexes and solvents were carried out under N_2 -atmosphere.

The 1H - and ^{13}C -NMR. spectra were measured in the *Fourier* transform mode at 100 MHz and 25.2 MHz, respectively, on *Varian XL-100* spectrometers using 5 and 10 mm sample tubes equipped with stopcock joints. C,C-coupling constants were also determined on a *Varian XL-200* instrument at 50.3 MHz with the aid of a spherical microcell placed in a 10 mm tube. The sample solutions (50–80%, v/v) were carefully prepared under N_2 -atmosphere. For the H-coupled ^{13}C -NMR. spectra a spectral width of 2000 Hz was used with an acquisition time of 8.187 seconds corresponding to 8 data points per Hz in the *Fourier*-transformed spectra. Further details are described in [2]. For the determination of C,C-coupling constants H-noise-decoupled ^{13}C -NMR. spectra were measured on the XL-100 instrument with a spectral width of 2–3000 Hz using double precision accumulation (31 bit word length and 65K words), on the XL-200 using floating point *Fourier* transformation. The chemical shifts are given as δ in ppm.

(*Butadiene*)tricarbylosmium (**3**). The photochemical reaction of 1,3-butadiene with dodecacarbonyl-triosmium (*Strem Chemicals Inc.*) was carried out in tetrahydrofuran in an evacuated pyrex tube with a magnetic stirrer inside. The sample tube and the UV. lamp (*Philips* HPK 125 W) were surrounded by a water bath (80°). In a typical run 200 mg of osmiumcarbonyl with an excess of butadiene in 20 ml of solvent were irradiated for a period of 4 h. The completion of the reaction is indicated by the disappearance of solid metal carbonyl and the yellow color of the solution. After evaporation of the solvent (20°/10 Torr) the crude product was chromatographed (silica/pentane) to give complex **3** as a colorless solid, m.p. 22°. The yield relative to osmiumcarbonyl is 55%. - IR. (CCl_4): 2070s, 1995s, 1985s (cm^{-1}). - MS. (70 eV): 330 (100, M^+), 302 (78, $M^+ - CO$), 276 (90, $M^+ - C_4H_6$), 274 (93, $M^+ - 2 CO$), 248 (67), 246 (93, $M^+ - 3 CO$), 220 (17), 218 (47), 216 (53), 205 (47), 192 (17), 54 (40).

$C_7H_6O_3Os$ (328.3) Calc. C 25.61 H 1.84% Found C 25.91 H 1.92%

(*1,3-Pentadiene*)tricarbyliron (**4**) was purchased from *Strem Chemicals Inc.* and purified by chromatography. - ^{13}C -NMR.: 19.0 (CH_3), 39.4 (C(1)), 58.3 (C(4)), 81.1 (C(2)), 89.4 (C(3)), 212.7 (CO).

(*1,3-Pentadiene*)tricarbylruthenium (**5**) was obtained in the same way as **2** from 1,3-pentadiene and $Ru_3(CO)_{12}$ [3]. - ^{13}C -NMR.: 19.8 (CH_3), 31.6 (C(1)), 50.2 (C(4)), 82.1 (C(2)), 91.1 (C(3)), 198.3 (CO).

$C_8H_8O_3Ru$ (253.2) Calc. C 37.95 H 3.18% Found C 38.20 H 3.31%

(*1,3-Pentadiene*)tricarbylosmium (**6**) was synthesized in the same way as **3** from 1,3-pentadiene and $Os_3(CO)_{12}$. For the measurements of the C,C-coupling constants it was purified by HPLC. (silica/pentane). - ^{13}C -NMR.: 20.1 (CH_3), 23.6 (C(1)), 40.8 (C(4)), 78.1 (C(2)), 87.9 (C(3)). The carbonyl resonances could not be observed at ambient temperature. - MS. (70 eV): 344 (36, M^+),

316 (48, $M^+ - CO$), 288 (23, $M^+ - 2 CO$), 286 (96), 260 (5, $M^+ - 3 CO$), 258 (90), 256 (100), 192 (89), 68 (11).

(Cyclohexadiene)tricarbonyliron (**7**) and (cyclohexadiene)tricarbonylruthenium (**8**) were prepared according to [17] and [18] respectively. Complex **7** is also commercially available.

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