

SUBSTITUTED DERIVATIVES OF TRIS(BUTADIENE)-MOLYBDENUM AND -TUNGSTEN; THE MOLECULAR STRUCTURES OF $(\text{CH}_2=\text{CMeCMe}=\text{CH}_2)_3\text{M}$ (M = Mo, W)

BORISLAV BOGDANOVIĆ, HELMUT BÖNNEMANN, RICHARD GODDARD,
ANATOLII STARTSEV and JULIAN M. WALLIS

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim-Ruhr (F.R.G.)

(Received July 8th, 1985)

Summary

Tris(substituted butadiene) complexes of molybdenum and tungsten have been prepared by the reduction of the metal halides with anthracene-activated magnesium in the presence of the appropriate diene. An X-ray diffraction study has shown tris(2,3-dimethylbutadiene)molybdenum and its tungsten analogue to be isomorphous, with each diene unit displaying a long–short–long bond alternation, and having short metal to terminal carbon atom distances, in marked contrast to the unsubstituted complexes.

Introduction

Tris(η^4 -butadiene)molybdenum and tungsten were first prepared by Skell et al. by the co-condensation of the metal vapours with butadiene [1]. Wilke and Gausing [2] subsequently devised syntheses based on magnesium reduction of the metal halides in the presence of butadiene. Although the crystal structure of tris(butadiene)-molybdenum has been reported [1], the exact nature of the bonding in this molecule is still unclear, and theoretical calculations have suggested [3] that the geometry of the metal-bound diene should display distortions not observed in the solid state structure.

We describe here syntheses of tris(substituted diene)-molybdenum and -tungsten complexes using anthracene activated magnesium [4], and X-ray structural determinations on tris(2,3-dimethylbutadiene)-molybdenum and -tungsten.

Results

Treatment of molybdenum pentachloride with anthracene-activated magnesium in the presence of a conjugated diene (L) gives, on work-up, the corresponding homoleptic diene complexes tris(butadiene)molybdenum (I, L = butadiene), tris(isoprene)molybdenum (II, L = isoprene) or tris(2,3-dimethylbutadiene)molybdenum (III, L = 2,3-dimethylbutadiene). Similar treatment of tungsten hexachloride gives

TABLE 1
REACTION CONDITIONS AND YIELDS OF I-VI

Metal halide	Diene	Product	Molar ratios M/Mg/L./Anthr.	Reaction time (h) ^a	Subl. temp. (°C) ^b	Colour
MoCl ₅	butadiene	I	1/3.9/7.0/0.10	4	—	brown
	isoprene	II	1/4.8/4.8/0.05 1/5.3/6.8/0.04	24 48	70 60	green-brown
	2,3-dimethylbutadiene	III	1/5.7/7.0/0.02	6	120	yellow
WCl ₆	butadiene	IV	1/5.0/10.0/0.10	24	120	yellow
	isoprene	V	1/4.8/4.4/0.10	24	80	green-brown
	2,3-dimethylbutadiene	VI	1/6.6/8.1/0.05 1/4.7/8.3/0.05	4 24	120 120	yellow

^a Reaction time at room temperature. ^b At 10⁻⁴ Torr.

the analogous complexes tris(butadiene)tungsten, (IV), tris(isoprene)tungsten (V) or tris(2,3-dimethylbutadiene)tungsten (VI). The conditions and yields of the reactions are summarised in Table 1.

The butadiene complexes I and IV were obtained as yellow-brown crystals from tetrahydrofuran, and were characterised by comparison of their spectroscopic properties with those reported [5]. These complexes, like their dimethylbutadiene analogues III and VI, are stable in air for a week or more.

Complexes II and V are green-brown oils at room temperature, and do not solidify at -78°C. They are volatile and readily soluble in organic solvents, but decompose slowly at room temperature, both in solution and in free state.

The compounds I-VI show characteristic coordinated double bond resonances in the region 1525-1500 cm⁻¹ in the infrared spectra, together with *sp*² C-H stretching vibrations at 3030-3020 cm⁻¹.

In the ¹H NMR spectra, the four terminal hydrogen atoms of the coordinated diene unit appear to high field of those from the internal C-H bonds, which appear at ca. 4-5 ppm. In the region δ 1.5 to δ -0.5 two distinct groups of signals may be assigned as *exo*-H (to lower field) and *endo*-H (to higher field). The ¹³C NMR spectra are similar, with the internal carbon atoms showing shifts in the range 100-120 ppm, and the terminal CH₂ groups in the region 30-45 ppm. There is a gradual shift of all of the resonances to low field upon substitution with methyl groups. The ¹³C NMR spectra of the tris(isoprene) derivatives are somewhat complex, with each resonance group consisting of four patterns of approximately equal integrals; we attribute this behaviour to the presence of an equilibrium between two stereoisomers (ratio 3/1) of II (or V) in solution.

In all cases the reduction reaction is accompanied by polymerisation of the tetrahydrofuran solvent, which limits the yields of the reactions. This is presumably caused by the presence of the catalytic system MCl_n/Mg, since polymerisation is observed in the absence of diene at -10°C. Attempts to improve the yield by using other solvents (toluene, diethyl ether) were unsuccessful.

TABLE 2
CRYSTAL DATA FOR THE X-RAY STRUCTURAL ANALYSES

Formula	C ₁₈ H ₃₀ Mo	C ₁₈ H ₃₀ W
<i>M</i> (a.m.u.)	342	430
<i>a</i> (Å)	7.080(1)	7.070(1)
<i>b</i> (Å)	9.579(2)	9.604(2)
<i>c</i> (Å)	12.354(1)	12.362(1)
α (°)	99.02(1)	99.29(1)
β (°)	97.64(1)	97.57(1)
γ (°)	90.38(1)	90.26(1)
<i>V</i> (Å ³)	819.84	820.86
<i>T</i> (°C)	18	18
<i>Z</i>	2	2
Crystal class	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>D</i> _c (g cm ⁻³)	1.39	1.74
μ (Mo- <i>K</i> α) (cm ⁻¹)	7.68	71.7
<i>R</i>	0.023	0.039
<i>R</i> _w	0.028	0.049
Total no. of reflns.	3888 ($\pm h, \pm k, +l$)	4733 ($\pm h, \pm k, +l$)
Obs. refl. ($I \geq 2\sigma(I)$), <i>NO</i>	3600	4033
Number of variables, <i>NV</i>	292	172
Error of fit,		
$[\sum w(F_o - F_c)^2 / NO - NV]^{0.5}$	1.66	2.34
Absorption correction:		
<i>A</i> _{max} , <i>A</i> _{min}	—	5.88, 1.81
$\theta_{\min}$, $\theta_{\max}$ (°)	1.68, 29.88	1.68, 29.9
Shift/error in the		
final cycle	0.004	0.007
Final diff. Fourier (e Å ⁻³)	0.8	3.2

In the reaction with 1,3-pentadiene, red-brown sublimable materials are formed, which are indicated by infrared and mass spectroscopies to contain the corresponding tris(1,3-pentadiene)-molybdenum and -tungsten species. These compounds have yet to be isolated pure.

X-Ray crystallographic analysis of III and VI

Complexes III and VI crystallise in the triclinic space group *P* $\bar{1}$ as isomorphous yellow needles. Crystal data are given in Table 2. The results of the structure determinations are summarised in Tables 3 and 4, which give the atomic fractional coordinates for III and VI, respectively. Within experimental error the molecular structures of III and VI are equivalent, with each molecule containing a non-crystallographic three-fold axis, leading to a trigonal prismatic geometry about the metal centre (Fig. 1). Important bond lengths and angles for III and VI are shown in Table 5*.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and further information on the data collection have been deposited with the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (F.R.G.), and may be obtained on request by submission of the deposition number CSD 51491, the names of the authors, and the full literature citation for this paper.

TABLE 3

ATOMIC FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR III ($U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$; where U_i are the eigenvalues of the U_{ij} matrix)

Atom	x	y	z	U_{eq}
Mo	0.2429(1)	0.3321(1)	0.2306(1)	0.027
C(1)	0.1528(3)	0.3815(2)	0.4003(1)	0.040
C(2)	0.2497(2)	0.2506(2)	0.4052(1)	0.038
C(3)	0.4355(2)	0.2441(2)	0.3787(1)	0.038
C(4)	0.5164(3)	0.3686(2)	0.3488(1)	0.041
C(5)	0.1512(3)	0.1262(2)	0.4372(2)	0.049
C(6)	0.5500(3)	0.1122(3)	0.3799(2)	0.051
C(11)	0.0186(3)	0.1581(2)	0.1929(1)	0.040
C(12)	0.0472(2)	0.1817(1)	0.0839(1)	0.036
C(13)	0.2338(2)	0.1749(2)	0.0580(1)	0.036
C(14)	0.3816(3)	0.1446(2)	0.1425(1)	0.040
C(15)	-0.1193(3)	0.2138(2)	0.0024(2)	0.045
C(16)	0.2809(4)	0.1980(3)	-0.0538(1)	0.049
C(21)	0.0108(3)	0.4748(2)	0.1749(1)	0.039
C(22)	0.1496(3)	0.5740(2)	0.2414(1)	0.038
C(23)	0.3365(3)	0.5692(2)	0.2156(1)	0.039
C(24)	0.3758(3)	0.4658(2)	0.1246(1)	0.040
C(25)	0.0929(4)	0.6778(2)	0.3557(2)	0.051
C(26)	0.4926(4)	0.6676(2)	0.2810(2)	0.051
H(11)	0.208(3)	0.467(3)	0.432(2)	0.045
H(12)	0.026(4)	0.382(3)	0.409(2)	0.051
H(41)	0.637(4)	0.360(3)	0.323(2)	0.060
H(42)	0.505(3)	0.459(3)	0.390(2)	0.045
H(51)	0.023(4)	0.133(3)	0.427(2)	0.068
H(52)	0.181(4)	0.041(3)	0.393(2)	0.063
H(53)	0.190(4)	0.124(3)	0.516(2)	0.062
H(61)	0.464(5)	0.030(4)	0.351(3)	0.084
H(62)	0.645(5)	0.108(3)	0.327(3)	0.088
H(63)	0.604(4)	0.106(3)	0.450(3)	0.071
H(111)	-0.105(4)	0.174(3)	0.213(2)	0.049
H(112)	0.069(3)	0.078(3)	0.221(2)	0.046
H(141)	0.505(4)	0.153(3)	0.128(2)	0.051
H(142)	0.366(4)	0.067(3)	0.182(2)	0.050
H(151)	-0.092(4)	0.271(3)	-0.045(2)	0.050
H(152)	-0.222(4)	0.258(3)	0.040(2)	0.064
H(153)	-0.168(4)	0.133(3)	-0.038(2)	0.072
H(161)	0.403(4)	0.225(3)	-0.052(2)	0.065
H(162)	0.248(4)	0.113(3)	-0.106(3)	0.079
H(163)	0.212(4)	0.270(3)	-0.083(2)	0.071
H(211)	0.004(4)	0.463(3)	0.102(2)	0.052
H(212)	-0.118(4)	0.475(3)	0.198(2)	0.056
H(241)	0.513(3)	0.455(2)	0.115(2)	0.041
H(242)	0.291(4)	0.459(3)	0.061(2)	0.051
H(251)	0.182(4)	0.693(3)	0.398(2)	0.069
H(252)	0.068(4)	0.765(3)	0.309(2)	0.072
H(253)	-0.015(4)	0.645(3)	0.362(2)	0.068
H(261)	0.480(4)	0.763(3)	0.257(2)	0.065
H(262)	0.615(5)	0.636(3)	0.271(2)	0.076
H(263)	0.484(4)	0.684(3)	0.357(2)	0.071

TABLE 4

ATOMIC FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR VI ($U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$; where U_i are the eigenvalues of the U_{ij} matrix)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
W	0.2429(1)	0.3318(1)	0.2298(1)	0.027
C(1)	0.151(1)	0.3831(8)	0.3984(5)	0.040
C(2)	0.252(1)	0.2481(8)	0.4044(5)	0.038
C(3)	0.435(1)	0.2416(9)	0.3773(5)	0.040
C(4)	0.514(1)	0.3705(9)	0.3472(6)	0.041
C(5)	0.150(1)	0.1205(9)	0.4348(7)	0.048
C(6)	0.552(1)	0.106(1)	0.3773(7)	0.048
C(11)	0.022(1)	0.1579(8)	0.1930(6)	0.038
C(12)	0.046(1)	0.1822(7)	0.0799(5)	0.037
C(13)	0.232(1)	0.1749(8)	0.0549(5)	0.039
C(14)	0.383(1)	0.1456(8)	0.1427(6)	0.039
C(15)	−0.123(1)	0.2144(9)	−0.0014(6)	0.043
C(16)	0.281(1)	0.2022(9)	−0.0586(6)	0.047
C(21)	0.010(1)	0.4736(7)	0.1747(6)	0.037
C(22)	0.150(1)	0.5753(7)	0.2418(6)	0.039
C(23)	0.334(1)	0.5701(8)	0.2173(6)	0.041
C(24)	0.376(1)	0.4633(8)	0.1254(6)	0.040
C(25)	0.091(1)	0.6798(9)	0.3397(7)	0.050
C(26)	0.494(1)	0.6692(9)	0.2858(7)	0.052

Experimental details. Nonius CAD-4 diffractometer with graphite monochromator, using Mo- K_{α} X-radiation (λ 0.71069 Å). θ – 2θ scan technique (96 steps). Scan speed variable: 1.3–5.0° min^{−1} depending on the standard deviation to intensity ratio of a preliminary 5.0° min^{−1} scan. The intensity of a reflection and its standard deviation were calculated from $\text{INT}-2(\text{BGL} + \text{BGR})/\text{Lp}$ and $[\text{INT} + 4(\text{BGL} + \text{BGR})]^{0.5}/\text{Lp}$, where INT, BGL and BGR are the peak intensity, the left and the right backgrounds, respectively, Lp the Lorentz and polarisation correction, and the time spent measuring the background was half that taken to measure the peak. $\sigma(F_0) = [\sigma^2(I)_{\text{Poisson}} + (Ik)^2]^{0.5}/2F$, $k = 0.02$. Horizontal detector aperture: 4.0 + 1.0 tan θ mm. Vertical aperture: 4.0 mm. (ω)scan range: 0.7 + 0.14 tan θ °. Cell parameters were obtained by a least-squares fit to the θ values of 75 automatically centred reflections. The structures were solved by Patterson (W and Mo) and Fourier methods (C and H for III, C for VI). Hydrogen atom positions were calculated for VI and included in the refinement with U_{H} 0.05 Å². Refinement was by least-squares, whereby the function minimised was $\sum w(F_0 - k|F_c|)^2$ with $w = 1.0/\sigma^2(F_0)$. Scattering factors were taken from International Tables for X-ray Crystallography and corrections for the effects of anomalous scattering for W and Mo were included in the structure factor calculations.

Discussion

The normal bond alternation observed in free conjugated dienes is reversed in these compounds, with long external C–C bonds (average 1.440(3) Å, III; 1.48(1) Å, VI), and shortened internal C–C bonds (average 1.400(3) Å, III; 1.38(1) Å, VI). The dimethylbutadiene ligands are planar (± 0.05 Å), and the planes of the ligands show

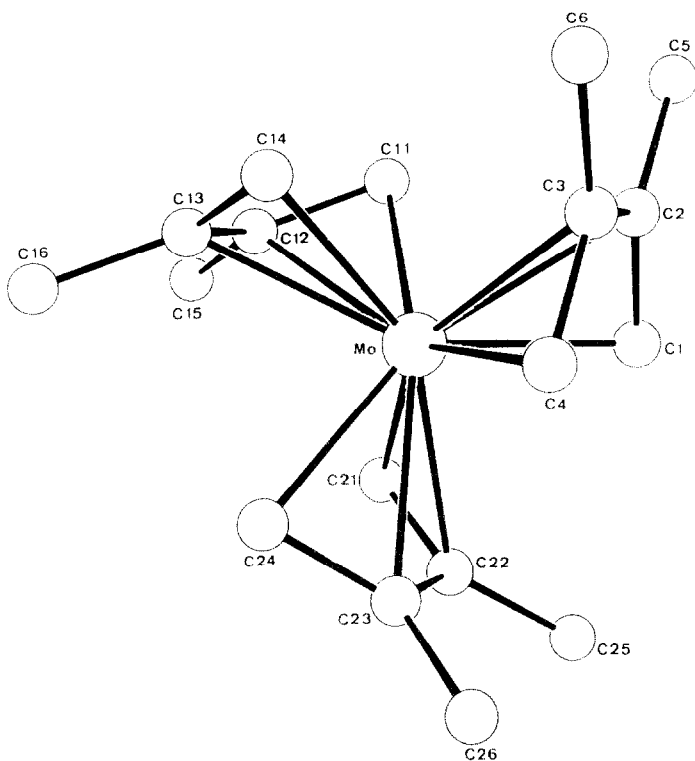


Fig. 1. The molecular structure of tris(2,3-dimethylbutadiene)molybdenum (III) showing the arbitrary numbering scheme. The hydrogen atoms have been omitted for clarity. Crystals of VI are isomorphous.

dihedral angles of $120.0(7)^\circ$, as expected from the molecular C_{3h} axis. The four metal bound carbon atoms of each diene unit are not symmetrically displaced from the metal centre; the external carbon atoms (C(1), C(4)) are significantly closer to the metal centre (average $2.252(3)$ Å, III; $2.24(1)$ Å, VI) than the internal carbon atoms (C(2), C(3)) of the fragment (average $2.402(2)$ Å, III; $2.42(1)$ Å, VI).

Upon coordination to a metal centre, diene fragments show a remarkable range of geometries. At one extreme, in tris(butadiene)molybdenum [1], the carbon–carbon bond lengths show the same alternation as in free butadiene, whilst in $\text{Cp}_2\text{Zr}(2,3\text{-dimethylbutadiene})$ [6] for example, the alternation is reversed. In the intermediate case of tris(*o*-xylidene)tungsten [7] the diene unit contains three approximately equal carbon–carbon bond distances.

It has been noted [8] that the magnitude of the two-bond geminal H–H coupling constant in the terminal carbon atoms of coordinated dienes can be related to the degree of rehybridisation towards sp^3 . In complexes with a greater degree of sp^3 character in the terminal C–H bonds, $^2J(\text{H,H})$ is expected to increase. The appropriate values for III–VI have been measured, and are compared to those of the unsubstituted diene complexes in Table 6.

The C–C bond lengths in (butadiene)irontricarbonyl were found to be the same within experimental error [9], as was found for I. Correspondingly, the geminal H–H coupling constant was found to be 2.42 Hz [10], in good agreement with that for I.

TABLE 5
BOND DISTANCES (Å) AND ANGLES (°) FOR III AND VI

<i>Distances and angles for III</i>					
Mo–C(1)	2.254(2)	Mo–C(11)	2.246(2)	Mo–C(21)	2.251(2)
Mo–C(2)	2.402(2)	Mo–C(12)	2.402(2)	Mo–C(22)	2.403(2)
Mo–C(3)	2.399(2)	Mo–C(13)	2.403(2)	Mo–C(23)	2.404(2)
Mo–C(4)	2.255(2)	Mo–C(14)	2.251(2)	Mo–C(24)	2.254(2)
C(1)–C(2)	1.439(3)	C(11)–C(12)	1.440(3)	C(21)–C(22)	1.440(3)
C(2)–C(3)	1.396(3)	C(12)–C(13)	1.401(3)	C(22)–C(23)	1.402(3)
C(3)–C(4)	1.440(3)	C(13)–C(14)	1.442(3)	C(23)–C(24)	1.436(3)
C(2)–C(5)	1.508(4)	C(12)–C(15)	1.512(3)	C(22)–C(25)	1.508(4)
C(3)–C(6)	1.508(4)	C(13)–C(16)	1.512(3)	C(23)–C(26)	1.508(4)
C(1)–C(2)–C(3)	117.5(2)	C(11)–C(12)–C(13)	117.3(2)	C(21)–C(22)–C(23)	117.7(2)
C(1)–C(2)–C(5)	120.4(2)	C(11)–C(12)–C(15)	120.5(2)	C(21)–C(22)–C(25)	120.2(2)
C(3)–C(2)–C(5)	122.1(2)	C(13)–C(12)–C(15)	122.2(2)	C(23)–C(22)–C(25)	122.0(2)
C(4)–C(3)–C(6)	120.1(2)	C(14)–C(13)–C(16)	120.7(2)	C(24)–C(23)–C(26)	120.6(2)
C(2)–C(3)–C(4)	117.8(2)	C(12)–C(13)–C(14)	117.4(2)	C(22)–C(23)–C(24)	117.6(2)
C(2)–C(3)–C(6)	122.1(2)	C(12)–C(13)–C(16)	122.0(2)	C(22)–C(23)–C(26)	121.7(2)
C(1)–Mo–C(4)	74.6(1)	C(11)–Mo–C(14)	74.5(1)	C(21)–Mo–C(24)	74.8(1)
C(1)–Mo–C(2)	35.8(1)	C(11)–Mo–C(12)	35.9(1)	C(21)–Mo–C(22)	35.8(1)
C(4)–Mo–C(3)	35.9(1)	C(14)–Mo–C(13)	35.9(1)	C(24)–Mo–C(23)	35.7(1)
C(2)–Mo–C(3)	33.8(1)	C(12)–Mo–C(13)	33.9(1)	C(22)–Mo–C(23)	33.9(1)
C(1)–Mo–C(11)	87.4(1)	C(11)–Mo–C(21)	86.4(1)	C(21)–Mo–C(1)	87.0(1)
C(1)–Mo–C(14)	133.1(1)	C(11)–Mo–C(24)	133.2(1)	C(21)–Mo–C(4)	133.6(1)
C(4)–Mo–C(11)	133.4(1)	C(14)–Mo–C(21)	133.0(1)	C(24)–Mo–C(1)	132.6(1)
C(4)–Mo–C(14)	87.0(1)	C(14)–Mo–C(24)	87.7(1)	C(24)–Mo–C(4)	87.0(1)
<i>Distances and angles for VI</i>					
W–C(1)	2.243(7)	W–C(11)	2.233(8)	W–C(21)	2.247(8)
W–C(2)	2.416(7)	W–C(12)	2.423(7)	W–C(22)	2.419(8)
W–C(3)	2.407(8)	W–C(13)	2.420(7)	W–C(23)	2.410(8)
W–C(4)	2.237(7)	W–C(14)	2.241(8)	W–C(24)	2.230(8)
C(1)–C(2)	1.49(1)	C(11)–C(12)	1.49(1)	C(21)–C(22)	1.46(1)
C(2)–C(3)	1.38(1)	C(12)–C(13)	1.39(1)	C(22)–C(23)	1.38(1)
C(3)–C(4)	1.48(1)	C(13)–C(14)	1.48(1)	C(23)–C(24)	1.46(1)
C(2)–C(5)	1.54(1)	C(12)–C(15)	1.52(1)	C(22)–C(25)	1.55(1)
C(3)–C(6)	1.54(1)	C(13)–C(16)	1.55(1)	C(23)–C(26)	1.54(1)
C(1)–C(2)–C(3)	117.0(7)	C(11)–C(12)–C(13)	115.6(6)	C(21)–C(22)–C(23)	117.6(7)
C(1)–C(2)–C(5)	120.7(7)	C(11)–C(12)–C(15)	121.4(6)	C(21)–C(22)–C(25)	120.1(7)
C(3)–C(2)–C(5)	122.3(7)	C(13)–C(12)–C(15)	123.0(7)	C(23)–C(22)–C(25)	122.2(7)
C(4)–C(3)–C(6)	121.3(7)	C(14)–C(13)–C(16)	121.3(7)	C(24)–C(23)–C(26)	120.9(7)
C(2)–C(3)–C(4)	116.7(7)	C(12)–C(13)–C(14)	117.3(7)	C(22)–C(23)–C(24)	117.4(7)
C(2)–C(3)–C(6)	122.0(7)	C(12)–C(13)–C(16)	121.4(7)	C(22)–C(23)–C(26)	121.7(7)
C(1)–W–C(4)	74.7(3)	C(11)–W–C(14)	74.5(3)	C(21)–W–C(24)	75.1(3)
C(1)–W–C(2)	37.0(3)	C(11)–W–C(12)	36.9(3)	C(21)–W–C(22)	36.2(3)
C(4)–W–C(3)	36.8(3)	C(14)–W–C(13)	36.8(3)	C(24)–W–C(23)	36.5(3)
C(2)–W–C(3)	33.2(3)	C(12)–W–C(13)	33.3(2)	C(22)–W–C(23)	33.2(3)
C(1)–W–C(11)	87.4(3)	C(11)–W–C(21)	86.8(3)	C(21)–W–C(1)	86.5(3)
C(1)–W–C(14)	133.4(3)	C(11)–W–C(24)	133.6(3)	C(21)–W–C(4)	133.1(3)
C(4)–W–C(11)	133.3(3)	C(14)–W–C(21)	133.4(3)	C(24)–W–C(1)	132.2(3)
C(4)–W–C(14)	87.1(3)	C(14)–W–C(24)	87.6(3)	C(24)–W–C(4)	86.5(3)

TABLE 6
ABSOLUTE MAGNITUDES OF $^2J(\text{H},\text{H})$ (Hz) IN I-VI

	Mo			W		
Complex	I	II	III	IV	V	VI
$J(\text{H},\text{H})$	2.98	3.4	3.7	4.46	4.7	5.2

Upon substitution, the magnitude of $^2J(\text{H}-\text{H})$ increases gradually, which is consistent with the crystallographic observation of increased distortion of the C-C bond lengths in III and VI.

Experimental

All reactions were carried out under argon.

^1H NMR and ^{13}C (^1H) NMR spectra were recorded on a Bruker WM400 at 400 MHz and 75.47 MHz, respectively, and were calibrated using the residual toluene- d_8 protio-solvent resonances; the atomic numbering scheme corresponds to that used in Fig. 1. Mass spectra were recorded on a Finnigan MAT CH5 (70 eV).

Tris(butadiene)molybdenum (I)

Magnesium powder (3.3 g, 0.14 mol) and anthracene (0.7 g, 3.9 mmol) were placed in a 0.5 l flask, and gently warmed together in vacuo. After cooling, tetrahydrofuran (200 cm³) and 2-3 drops of iodomethane were added, and a yellow-green solution of magnesium-anthracene resulted, after stirring at room temperature for 2-3 h. Molybdenum pentachloride (9.4 g, 34 mmol) was slowly added to the cooled (-78°C) stirred mixture, and butadiene (21 cm³, 0.24 mol) was siphoned into the flask. The mixture was allowed to warm very slowly to room temperature, and then stirred for 4 h. Removal of volatile components in vacuo left a brown oily residue; this was extracted with pentane (1 l), and the extract was then evaporated to dryness. Sublimation (10^{-4} Torr) of the residue gave a brown material, which upon crystallisation from tetrahydrofuran yielded yellow-brown needles of I. Yield 0.88 g, 9.7%.

The same method was used for the preparation of II-VI, with reaction conditions as summarised in Table 1.

Tris(isoprene)molybdenum (II)

Analysis: Found (calcd.) (%): C, 60.19 (59.99); H, 8.14 (8.05); Mo, 31.79 (31.95).

^1H NMR: 4.36 (1H, m, H(3)), 1.74 (3H, s, CH_3), 1.51 (1H, m, *exo*-H(4)), 1.26 (1H, m, *exo*-H(1)), 0.13 (1H, m, *endo*-H(1)), -0.01 (1H, m, *endo*-H(4)).

^{13}C (^1H) NMR: 115.91 (1C, m, C(2)), 102.11 (1C, m, C(3)), 46.40 (1C, m, C(1)), 40.52 (1C, m, C(4)), 23.39 (1C, m, CH_3).

Mass spectrum: 302 (M^+).

Tris(2,3-dimethylbutadiene)molybdenum (III)

Analysis: Found (calcd.) (%): C, 63.28 (63.14); H, 8.74 (8.83); Mo, 27.84 (28.02).

^1H NMR: 1.64 (6H, s, 2CH_3), 1.32 (2H, d, J 3.7 Hz, *exo*-H), -0.41 (2H, d, J 3.7 Hz, *endo*-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: 112.1 (2C, s, C(2), C(3)), 49.5 (2C, s, C(1), C(4)), 20.3 (2C, s, 2CH_3).

Mass spectrum: 344 (M^+).

Tris(butadiene)tungsten (IV)

Analysis: Found (calcd.) (%): C, 41.81 (41.64); H, 5.10 (5.25); W, 53.02 (53.12).

^1H NMR: 4.61 (2H, m, H(2), H(3)), 1.35 (2H, m, *exo*-H(1), H(4)), 0.26 (2H, m, *endo*-H(1), H(4)).

$^{13}\text{C}\{^1\text{H}\}$ NMR: 103.4 (2C, s, C(2), C(3)), 33.7 (2C, s, C(1), C(4)).

Tris(isoprene)tungsten (V)

Analysis: Found (calcd.) (%): C, 46.05 (46.40); H, 6.80 (6.24); W, 46.95 (47.35).

^1H NMR: 4.44 (1H, m, H(3)), 1.87 (3H, m, CH_3), 1.34 (1H, m, *exo*-H(4)), 1.09 (1H, m, *exo*-H(1)), 0.09 (2H, m, *endo*-H(1), H(4)).

$^{13}\text{C}\{^1\text{H}\}$ NMR: 116.66 (1C, m, C(2)), 102.42 (1C, m, C(3)), 41.06 (1C, m, C(1)), 34.45 (1C, m, C(4)), 22.91 (1C, m, CH_3).

Mass spectrum: 388 (M^+).

Tris(2,3-dimethylbutadiene)tungsten (VI)

Analysis: Found (calcd.) (%): C, 50.36 (50.24); H, 6.94 (7.03); W, 42.64 (42.73).

^1H NMR: 1.74 (6H, s, 2CH_3), 1.13 (2H, d, J 5.2 Hz, *exo*-H(1), H(4)), -0.33 (2H, s, *endo*-H(1), H(4)).

$^{13}\text{C}\{^1\text{H}\}$ NMR: 111.6 (2C, s, C(2), C(3)), 44.2 (2C, s, C(1), C(4)), 20.0 (2C, s, 2CH_3).

Mass spectrum: 430 (M^+).

Acknowledgements

A.S. and J.M.W. thank the Max-Planck-Gesellschaft for Stipendia. Some of the work described in this paper was undertaken while A.S. was on leave from the Institute of Catalysis, Novosibirsk 630090 (U.S.S.R.). B.B., H.B. and A.S. thank Dr. R. Benn, Dr. R. Mynott and G. Schroth for helpful discussions about the ^1H and ^{13}C NMR spectra.

References

- 1 P.S. Skell, M.J. McGlinchey, *Angew. Chem.*, 87 (1975) 215.
- 2 W. Gausing, G. Wilke, *Angew. Chem.*, 93 (1981) 201.
- 3 J.C. Green, M.R. Kelly, P.D. Grebenik, C.E. Briant, N.A. McEvoy, D.M.P. Mingos, *J. Organomet. Chem.* 228 (1982) 239.
- 4 H. Bönemann, B. Bogdanović, DBP 3 205 550 (Prior. 17.02.82); Eur. Pat. 83 101 246.3 (10.02.83), Studiengesellschaft Kohle m.b.H.; H. Bönemann, B. Bogdanović, R. Brinkmann, D.-W. He.B. Spliethoff, *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 728.
- 5 P.W. Jolly, R. Mynott, *Adv. Organomet. Chem.* 19 (1982) 257.
- 6 G. Erker, K. Engel, C. Krüger, A.-P. Chiang, *Chem. Ber.* 115 (1982) 3311; G. Erker, K. Engel, C. Krüger, *Organometallics* 3 (1984) 128.
- 7 M.F. Lappert, C.L. Raston, B.W. Skelton, A.H. White, *J. Chem. Soc. Chem. Comm.* (1981) 485.
- 8 R. Benn, G. Schroth, *J. Organomet. Chem.* 228 (1982) 71.
- 9 O.S. Mills, G. Robinson, *Acta Cryst.*, 16 (1963) 758.
- 10 K. Bachmann, W. von Philipsborn, *Org. Mag. Res.* 8 (1976) 648.