Synthesis, Structure, and Properties of Homoleptic 1-Oxa-1,3-diene Molybdenum and Tungsten Complexes

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Dedicated to Prof. Dr. Dr. h.c. mult. Günther Wilke on the occasion of his 70th birthday

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Oxadiene Complex, Molybdenum, Tungsten, X-Ray, Selective Hydrogenation

Homoleptic tris(1-oxa-1,3-diene)molybdenum and tungsten complexes are formed as yellow, crystalline compounds in 54–80% isolated yield on treatment of the corresponding \(\eta^4\)-unsaturated ketones with W(CO)\(_3\)(CH\(_2\)(CH\(_2\)CN)) or (\(\eta^5\)-C\(_5\)H\(_5\)Me)Mo(CO)\(_3\)), in refluxing hexane. Reaction of these oxadienes with (\(\eta^4\)-C\(_5\)H\(_5\)CH\(_2\))Mo in tetrahydrofuran or n-hexane provides a new high yield route to homoleptic molybdenum complexes that are otherwise difficult to prepare. X-ray crystal structure analyses of two air-stable, isomeric tungsten complexes reveal a significant contribution of a \(\sigma^2\eta^2\)-bonding mode in the coordinated oxadiene moieties. Under reaction conditions that allow the platinum catalyzed hydrogenation of phenyl substituents in these ligands, the coordinated oxadiene fragments are inert, thus demonstrating an unprecedented chemoselectivity in the hydrogenation of aryl-substituted enones. On the other hand, the complexes are labile enough to catalyze the cyclotrimerization of alkynes such as methyl propiolate.

Homoleptic diene complexes of molybdenum and tungsten were first prepared by Skell et al. [1] using metal vapour techniques in 1974, but multi-gram quantities of these compounds with butadiene and methylated butadienes as ligands became available only later with the more efficient procedure of Wilke and Gausing [2] and Bogdano-vic et al. [3]. Similarly, for more than two decades the only (1-oxa-1,3-diene)\(_3\)M compounds were the complexes of but-3-en-2-one (methylvinyl ketone) prepared by King and Fronzaglia [4]. Apart from a crystal structure [5], almost no additional information on these compounds, and in particular on their reactivity, has been published since then. The reason might be the poor 1.9% yield reported for the molybdenum complex.

The structure of diene as well as the oxadiene compounds (X = CH\(_2\), O) of the composition ML\(_3\) has been discussed (e.g. [4, 5]) both in terms of \(\eta^4\)- and \(\sigma^2\eta^2\)-bound ligands. Our recent investigations into bonding modes in bis(oxadiene) complexes [6] as well as literature data in comparison with the X-ray structural work reported here on the homoleptic complexes lead to further insights in this respect.

In a preliminary communication we reported an improved synthetic method [7] which allowed us to show that the ability to form homoleptic oxadiene complexes is not a unique property of the but-3-en-2-one ligand. Yields of 54–80% could be obtained with several \(\beta\)-unsaturated \(\alpha,\beta\)-unsaturated ketones, thus providing an easy route to gram quantities of these compounds for reactivity studies. Nevertheless, it still remained difficult to prepare the molybdenum complexes selectively in a reproducible way and with reasonable yields for ligands other than 1-phenylprop-2-en-1-one (I).

In the following, we report on a new and highly efficient method for the synthesis of homoleptic oxadiene molybdenum complexes, the X-ray structural investigations of two closely related, isomeric tungsten oxadiene complexes, and the results of preliminary reactivity studies on these compounds.

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Syntheses and Characterization

The preparation of homoleptic tungsten oxadiene complexes is most conveniently performed by treating the appropriate 1-oxa-1,3-diene with tricarbonyltris(propionitrile)tungsten in refluxing n-hexane. Thereby, up to 80% isolated yield of the complexes could be obtained in several cases after chromatography or extraction and crystallization [7]. A similar reaction producing a homoleptic molybdenum oxadiene complex from 1,6-benzene-tricarbonylmolybdenum in reasonable yield has so far only been successful in the case of 1-phenyl-prop-2-en-1-one (1). When the oxadienes 2 or 3 were used in such reactions, significant dimerization and polymerization of the oxadiene occurred instead, together with some formation of dicarbonylbis(oxadiene) complexes [8]. The formation of homoleptic complexes was also observed in such reactions but turned out not to be reproducible in our hands. The products could only be separated with difficulty.

Since the most intriguing feature of these syntheses is the fact that all the carbonyl ligands attached to the metals – together with all the other ligands – are replaced by oxadienes, it appeared to be advantageous to use a starting complex with more weakly bound ligands in order to achieve a more facile replacement. For this purpose, we decided to investigate bis(arene)molybdenum complexes in more detail. Specifically, bis-(1-toluene)molybdenum turned out to be easily accessible on a multigram scale using a procedure originally already developed by Fischer et al. [9] for arene complexes of several metals, but later improved by Calderazzo et al. [10]. With some additional modifications [8], the bis-toluene complex could be obtained in up to 70% yield from molybdenum pentachloride.

On mixing a suspension of this complex in THF with oxadienes, e.g. but-3-en-2-one (4), immediate reaction occurred as indicated by a marked colour change from green to yellow-brown, and tris-(butenone)molybdenum (8a) was formed in excellent yield (69% isolated). Only little oligomerization of the highly reactive butenone was observed. Although not all the reactions investigated proceed as smoothly as the above example, the reaction procedure turned out to be quite general. Consequently, the complexes 6a and 7a

![Diagram](1)

<table>
<thead>
<tr>
<th>Oxadiene</th>
<th>R¹</th>
<th>R₂</th>
<th>Method</th>
<th>M</th>
<th>Complex</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>H</td>
<td>A</td>
<td>Mo</td>
<td>5a</td>
<td>64</td>
<td>162 (d)</td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>H</td>
<td>B</td>
<td>Mo</td>
<td>5a</td>
<td>70</td>
<td>160 (d)</td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>H</td>
<td>C</td>
<td>W</td>
<td>5b</td>
<td>80</td>
<td>160 (d)</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>Me</td>
<td>B</td>
<td>Mo</td>
<td>6a</td>
<td>54</td>
<td>169–170 (d)</td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>Me</td>
<td>C</td>
<td>W</td>
<td>6b</td>
<td>65</td>
<td>165 (d)</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>Ph</td>
<td>B</td>
<td>Mo</td>
<td>7a</td>
<td>62</td>
<td>180 (d)</td>
</tr>
<tr>
<td></td>
<td>Me</td>
<td>Ph</td>
<td>C</td>
<td>W</td>
<td>7b</td>
<td>57</td>
<td>190 (d)</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>H</td>
<td>B</td>
<td>Mo</td>
<td>8a</td>
<td>69</td>
<td>153–154</td>
</tr>
</tbody>
</table>

* Methods: A – (η⁶-C₆H₆)Mo(CO)₃, n-hexane, 65 °C; B – (η⁶-C₆H₅CH₃)₂Mo, THF, reaction temperatures and times given in Experimental Section; C – (CH₃CH₂CN)₃W(CO)₃, n-hexane, 65 °C; *Yields reported correspond to a scale of 2.5–5 mmol. For reasons still under investigation, yields at larger scale (10–20 mmol) are usually lower; d compound 7a decomposes without melting; (d) indicates decomposition during melting.
could be prepared for the first time in pure form, and it was possible to improve the yield of compound 5a from 64% to about 70% by employing the new procedure. The results of different synthetic methods are summarized in Table I.

Oxadiene complexes 5 to 8 are yellow, crystalline compounds which are only sparingly soluble in saturated hydrocarbons. The solubility is higher in ethers and aromatics and increases even more in chlorinated solvents such as dichloromethane or chloroform. The tungsten compounds are air-stable for prolonged periods of time, whereas all the molybdenum complexes darken after some hours in air and slowly decompose. Solutions, especially of the molybdenum complexes, are much more sensitive to decomposition. From the NMR spectra, the threefold symmetry of all the complexes reported here is directly obvious, as only one set of ligand signals can be found in the spectra. Comparison of the $^{13}$C NMR data (Table II) reveals a remarkable similarity of the shift values obtained for molybdenum and tungsten complexes with the same ligands ($\Delta\delta \lesssim 0.3$ ppm for $C_\alpha$ and $\Delta\delta \lesssim 4$ ppm for $C_\beta$). Only the carbonyl carbon resonance clearly allows a differentiation between molybdenum and tungsten compounds ($\Delta\delta 5.4-8.2$ ppm). This is in contrast to observations for bis(oxadiene) complexes (e.g. [6a]) where all the resonances of carbon atoms directly bound to a metal differ markedly for $M = Mo$ or $W$. Comparison with the resonances of the free oxadienes (Table II) indicates coordination shifts in the range of 21.5–39.4 ppm for the carbonyl carbon, 40.3–49.7 ppm for $C_\alpha$, and 54.9–74.7 ppm for $C_\beta$.

All tungsten complexes show remarkably large $^1J_{WC}$ couplings to the methylene carbon ($C_{\beta}$) of the oxadiene ligands (5b: 30.1 Hz; 6b: 34.4 Hz; 7b: 36.6 Hz). This parallels results already obtained for several dicarboxylbis(oxadiene)tungsten complexes, in which analogous coupling constants of 20 to 25 Hz are found [6c].

**X-Ray Crystal Structures of 6b and 7b**

One explanation for the remarkable stability of the homoleptic oxadiene complexes, especially for the lack of sensitivity to oxidative addition, e.g. when dissolved in halogenated solvents, is a bonding mode that is different from that found in normal $\pi$-bound $\eta^2$-diene complexes. As it is very difficult to deduce information on the coordination geometries from spectroscopic data, we decided to investigate two closely related complexes by X-ray crystallography in order to obtain reliable data on the bonding mode and to evaluate the effect of small changes in the molecular environment on the structure of such complexes.

Thus, the tungsten complexes 6b and 7b with isomeric ligands were subjected to X-ray crystal structure analyses. The results are summarized in Fig. 1 (6b) and 2 (7b). Neither of the complexes exhibits exact threefold symmetry in the solid state, presumably due to packing effects. However, there appears to be no significant change in the geometry of the coordinated oxadiene moieties caused by the formal exchange of methyl and phenyl substituents in the ligands attached to tungsten. The short M–O distances (average: 2.067(3) Å for 6b and 2.09(1) Å

<table>
<thead>
<tr>
<th>Oxadiene</th>
<th>M</th>
<th>Compound</th>
<th>Solvent</th>
<th>$C_\alpha$</th>
<th>$C_\beta$</th>
<th>$C_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>none</td>
<td>1</td>
<td>5a</td>
<td>5b</td>
</tr>
<tr>
<td>C=O</td>
<td>190.91</td>
<td>169.37</td>
<td>164.02</td>
<td>198.07</td>
<td>165.14</td>
<td>158.68</td>
</tr>
<tr>
<td>C_quart</td>
<td>137.39</td>
<td>135.39</td>
<td>134.80</td>
<td>137.55</td>
<td>135.27</td>
<td>134.55</td>
</tr>
<tr>
<td>$C_p$</td>
<td>132.82</td>
<td>131.65</td>
<td>131.41</td>
<td>132.82</td>
<td>130.49</td>
<td>130.22</td>
</tr>
<tr>
<td>$C_{om}$</td>
<td>128.61</td>
<td>129.33</td>
<td>129.29</td>
<td>129.20</td>
<td>130.98</td>
<td>130.67</td>
</tr>
<tr>
<td>$C_\alpha$</td>
<td>128.53</td>
<td>128.26</td>
<td>128.24</td>
<td>127.98</td>
<td>127.79</td>
<td>127.77</td>
</tr>
<tr>
<td>$C_\beta$</td>
<td>128.53</td>
<td>82.84</td>
<td>83.00</td>
<td>143.59</td>
<td>95.16</td>
<td>95.49</td>
</tr>
<tr>
<td>$C_m$</td>
<td>129.76</td>
<td>59.10</td>
<td>55.10</td>
<td>126.82</td>
<td>70.94</td>
<td>68.99</td>
</tr>
<tr>
<td>$C_{Me}$</td>
<td>18.44</td>
<td>19.81</td>
<td>19.59</td>
<td>27.31</td>
<td>21.98</td>
<td>20.81</td>
</tr>
</tbody>
</table>

for 7b) can be taken as one indication for a pronounced \(\sigma\)-character of this bond. These distances are already close to those typically found in tungsten alkoxides or enolates, \textit{i.e.} 1.88 to 2.10 \(\text{Å}\) [11]. The parallel arrangement of the three ligands around the central metal atom leads to an orthogonal orientation of all three oxygen atoms with respect to the metal, such that the O–M–O angles are always close to 90°. Similar O–M–O angles can be found in almost all the bis(oxadiene) [6] and bis(oxapentadienyl) complexes [12] we have looked at. This arrangement of oxygen atoms can be identified as a structural principle of oxadiene complexes.

In order to analyze the data with respect to the bonding quantitatively, geometrical data were first averaged over crystallographically independent molecules and symmetry independent ligands. In Table III, selected averaged distances are compared with those obtained for other oxadiene complexes with pronounced \(\pi\)-character in the metal-ligand interaction and with homoleptic diene complexes.

The distance difference, \(\Delta d\), which gives a measure of the hapticity, and the bond alternation difference, \(\Delta l\), which gives a measure of the delocalization of electron density, as defined in eq. (2) and (3) [13], most clearly reveal that these complexes fall into different groups of compounds. Whereas the bis(oxadiene) complexes 9 [6b] and 10 [6a] (X = O) are almost ideal \(\pi\)-complexes with \(\eta^2\)-bound ligands (typical \(\Delta d\): -0.1 to 0.1 \(\text{Å}\),...
Table III. Selected atomic distances\(^a\) [Å] of 1,3-diene and 1-oxa-1,3-diene complexes, distance difference \(\Delta d\) [Å] and bond alternation difference \(\Delta l\) [Å].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>M–X</th>
<th>M–C1</th>
<th>M–C2</th>
<th>M–C3</th>
<th>X–C1</th>
<th>C1–C2</th>
<th>C2–C3</th>
<th>(\Delta d)</th>
<th>(\Delta l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>[6b]</td>
<td>2.233(4)</td>
<td>2.388(5)</td>
<td>2.276(5)</td>
<td>2.260(5)</td>
<td>1.279(6)</td>
<td>1.404(7)</td>
<td>1.441(8)</td>
<td>−0.09</td>
<td>−0.04</td>
</tr>
<tr>
<td>10</td>
<td>[6a]</td>
<td>2.19(1)</td>
<td>2.381(8)</td>
<td>2.287(8)</td>
<td>2.328(9)</td>
<td>1.35(1)</td>
<td>1.432(11)</td>
<td>1.49(1)</td>
<td>−0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>11, M = Mo</td>
<td>[3]</td>
<td>2.250(2)</td>
<td>2.402(2)</td>
<td>2.402(2)</td>
<td>2.253(2)</td>
<td>1.440(3)</td>
<td>1.400(3)</td>
<td>1.439(3)</td>
<td>−0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>11, M = W</td>
<td>[3]</td>
<td>2.241(8)</td>
<td>2.419(7)</td>
<td>2.412(8)</td>
<td>2.236(8)</td>
<td>1.48(1)</td>
<td>1.38(1)</td>
<td>1.47(1)</td>
<td>−0.18</td>
<td>0.10</td>
</tr>
<tr>
<td>11, M = W</td>
<td>[5]</td>
<td>2.11(2)</td>
<td>2.42(2)</td>
<td>2.29(2)</td>
<td>2.12(2)</td>
<td>1.37(4)</td>
<td>1.32(4)</td>
<td>1.45(4)</td>
<td>−0.24</td>
<td>0.09</td>
</tr>
<tr>
<td>6b</td>
<td>this</td>
<td>2.067(3)</td>
<td>2.428(5)</td>
<td>2.386(5)</td>
<td>2.149(5)</td>
<td>1.345(6)</td>
<td>1.383(7)</td>
<td>1.468(7)</td>
<td>−0.30</td>
<td>0.02</td>
</tr>
<tr>
<td>7b</td>
<td>work</td>
<td>2.09(1)</td>
<td>2.47(1)</td>
<td>2.37(1)</td>
<td>2.14(1)</td>
<td>1.33(1)</td>
<td>1.39(2)</td>
<td>1.46(2)</td>
<td>−0.31</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(\Delta l\): −0.1 to 0 Å [13b]), the diene complexes 11 (X = CH\(_2\)) appear as borderline cases. The homoleptic oxadiene complexes, on the other hand, can already be classified as showing a pronounced \(\sigma^2,\eta^2\)-character of bonding (\(\Delta d\): −0.4 to 0 Å and \(\Delta l\): 0 to 0.2 Å).

\[
\Delta d = 0.5 \left[ d[M-X] + d[M-C3] \right] - 0.5 \left[ d[M-C1] + d[M-C2] \right] \quad (2)
\]

\[
\Delta l = 0.5 \left[ d[X-C1] + d[C2-C3] \right] - d[C1-C2] \quad (3)
\]

As can be deduced from Table III, \(\Delta l\) is only of limited worth for this evaluation, firstly because its calculation involved the averaging of an alkene and a carbonyl double bond distance, which might not lead to reasonable results at all, secondly, differences between most of the \(\Delta l\)-values in Table III are within experimental error of the data.

Another measure for the bonding character often used in the analysis of diene bonding, the folding angle (Fig. 3b) between the diene plane and the plane formed by the metal and the terminal diene carbon atoms, is less useful in the case of oxadienes, since the oxadiene moiety is significantly distorted from planarity in many cases (e.g. 18.7° \(\pi\)-oxadiene torsion angle in 10 [6a]), making it difficult to assign the planes necessary for angle calculation.

Reactivity

In the presence of various dienes or oxadienes, no ligand exchange could be observed with the homoleptic oxadiene complexes. That indeed the ligands are strongly bound to the metal can be further illustrated by results of hydrogenation experiments with complexes 5 to 7. Whereas sim-
pie heating of an ethereal solution of these compounds, e.g. $5\text{a}$ and $5\text{b}$, with hydrogen under pressure gave rise to the formation of an insoluble, metal containing solid along with the alkene reduction product 1-phenylpropan-1-one, attempts to perform hydrogenation reactions catalyzed by noble metals led to much more interesting results.

The reaction of the molybdenum complex $5\text{a}$ and the tungsten complex $6\text{b}$ may serve as examples. In the presence of platinum oxide at $35^\circ\text{C}$ the phenyl substituents at the metal-coordinated ligands of $5\text{a}$ could be smoothly reduced under hydrogen pressure (6 MPa) without decomposition of the complex or competing reduction of the oxadiene moiety (eq. (4)). It was found to be advantageous to add magnesium sulphate to the reaction mixture in order to remove traces of moisture from the autoclave walls and water arising from the reduction of the platinum dioxide. In these cases, complete conversion to the tris(cyclohexyl-oxadiene)metal complexes was observed. The tungsten compound $6\text{b}$ could be hydrogenated in an analogous procedure at $60^\circ\text{C}$ under 8 MPa of hydrogen pressure. In contrast to the complexes with aryl-substituted ligands, the resulting cyclohexyl complexes $12$ and $13$ are readily soluble in saturated hydrocarbons and can easily be recrystallized from them to yield pale-yellow crystals. They also exhibit threefold symmetry in solution, as is obvious from their NMR spectra.

As the ligands in $12$ and $13$ could easily be liberated from the metal by reaction with carbon monoxide under pressure ($85^\circ\text{C}; M = \text{Mo}; 6 \text{ MPa}; M = \text{W}; 10 \text{ MPa}$), the overall reaction sequence of complexation, hydrogenation and decomplexation results in a hitherto unprecedented hydrogenation selectivity. It is thus now possible to hydrogenate an aryl substituent in the presence of an $\alpha,\beta$-unsaturated ketone using the above procedure.

In order to demonstrate that, on the other hand, the coordinated oxadienes are not entirely inert, preliminary experiments were undertaken involving the cyclotrimerization of terminal alkynes such as hexyne-1, phenyl acetylene or methyl propiolate. These reactions are known to be catalyzed by a variety of transition metal compounds [14]. Although molybdenum complexes exhibit rather low catalytic activity in these reactions, this reactivity, which requires at least partial decoordination of the oxadiene ligands, was indeed observed for the homoleptic complexes (eq. (5)).

Control experiments with hexacarbonyl molybdenum proceeded much more slowly under comparable reaction conditions but ultimately lead to a similar 1:3 mixture of the trisubstituted arenes $15$ and $16$ with about 60% conversion.

**Experimental Section**

Preparation and handling of all the organometallic compounds, especially in solution and at elevated temperatures, was performed under an inert atmosphere of dried and purified argon using standard Schlenk techniques. The solvents were purified prior to use by standard procedures, usu-
ally employing Na[AlEt4] as drying agent, and subsequently saturated with argon. – Melting points were determined in capillary tubes sealed under argon and are uncorrected. $\eta^6$-Benzenetricarbonyl-
molybdenum(0) [15], tricarbonyltrim(pipino-
nitride)tungsten(0) [16] and bis($\eta^6$-toluene)molybdenum [10] were prepared by modifications of published methods. 1-Oxadienes 1 and 2 were ob-
published in our published procedure [7].

NMR spectra were recorded on spectrometers Bruker AM 200 (200.1 MHz $[^1]$H, 50.3 MHz $[^{13}$C]) or AMX 400 (400.134 MHz $[^1]$H, 100.614 MHz $[^{13}$C]), solvent signals were used as internal standards. Signal multiplicities obtained from DEPT experiments are given in brackets after the shift values. Mass spectra were obtained using a Varian 311 A spectrometer (for metal containing ions, sig-
als corresponding to the major isotopes $^{98}$Mo and $^{184}$W are reported), IR spectra from a Nicolet 7199 FT-IR instrument. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr.

**Tris(2-methyl-1-phenylprop-2-en-1-one)-
 molybdenum (6a)**

To a stirred, green suspension of 700 mg (2.5 mmol) of bis($\eta^6$-toluene)molybdenum in 12 ml of THF a solution of 1168 mg (8.0 mmol) of 2-methyl-1-phenylprop-2-en-1-one (2) in 3 ml of THF is added dropwise at room temperature. The colour of the suspension slowly changes to olive-
brown. After 60 h at 20 $^\circ$C, the toluene complex has completely disappeared. The volatile com-
ponents of the reaction mixture are removed under reduced pressure (10 Pa), the yellow-brown residue is extracted with three 20 ml portions of di-
ethyl ether. The combined extracts are filtered through a plug of silica (length: 8 cm/diameter 2.5 cm) with ether, the yellow-brown filtrate is evaporated under vacuum and the residue washed twice with 5 ml portions of pentane at $-30$ $^\circ$C. The washing solutions are decanted off and discarded, leaving behind after drying under high vacuum (10$^{-2}$ Pa) a yellow, crystalline residue of analyti-

cally pure 6a, which can be recrystallized from diethyl ether.

Yield: 720 mg (1.35 mmol, 54%): m.p. 169–
170 $^\circ$C (decomp.); $[^1]$H NMR (CDCl$_3$): $\delta$ 7.95–7.83 (m, 3 $\times$2H, $\text{H}_{\text{ph, ortho}}$), 7.44–7.30 (m, 3 $\times$3H, $\text{H}_{\text{ph, meta, para}}$), 2.43 (d, 3 $\times$1H, =CH$_2$, $^2$J$\text{HH} =$ 2.8 Hz), 2.09 (s, 3 $\times$3H, $\text{H}_{\text{Me}}$), 1.77 (d, 3 $\times$1H, = CH$_2$); $[^{13}$C NMR: see Table II; IR (KBr): $\nu$ 3060 (m), 3023 (m), 2960 (s), 2940 (m), 1600 (w), 1500 (m), 1472 (s), 1429 (m) 1419 (m), 1348 (m), 781 (m), 697 (s) cm$^{-1}$; MS (EI): $m/z$ (rel. int. [%]) 536 (M$^+$, 1%), 390 (4), 105 (100), 76 (32).

**Analysis for C$_{20}$H$_{20}$MoO$_3$**

Calcd C 67.41 H 5.66 Mo 17.95%.

Found C 67.24 H 5.76 Mo 17.82%.

**Tris(3-phenylbut-3-en-2-one)molybdenum (7a)**

A solution of 1131 mg (7.75 mmol) 3-phenyl-
but-3-en-2-one (3) in 5 ml of THF is added to a stirred suspension of 700 mg (2.5 mmol) of bis-
($\eta^6$-toluene)molybdenum in 12 ml of THF at room temperature. The reaction mixture is heated to
55 $^\circ$C for 48 h. Then it is evaporated to dryness under reduced pressure, exposed to air for 30 sec
to destroy the small amount of the toluene com-
plex still present, and then extracted with tetra-
chloromethane (5$x$10 ml). On evaporation of the filtered extracts, a yellow powder of analytically
pure 7a is obtained, which can be recrystallized
from diethyl ether or tetrachloromethane.

Yield: 828 mg (1.55 mmol, 62%); decomp. start-
ing at 180 $^\circ$C; $[^1]$H NMR (CDCl$_3$): $\delta$ 7.22–7.03 (m, 3 $\times$5H, $\text{H}_{\text{ph}}$), 2.26 (s, 3 $\times$3H, $\text{H}_{\text{Me}}$), 2.22 (d, 3 $\times$1H, =CH$_2$, $^2$J$\text{HH} =$ 3.5 Hz), 1.24 (d, 3 $\times$1H, =CH$_2$); $[^{13}$C NMR: see Table II; IR (KBr): $\nu$ 3058 (m), 3019 (m), 2979 (m), 2961 (w), 2918 (w), 1598 (m), 1499 (m), 1467 (s), 1408 (s), 1371 (s), 1300 (m), 768 (s), 703 (s) cm$^{-1}$; MS (EI): $m/z$ (rel. int. [%]) 536 (M$^+$, 8%), 390 (100), 242 (27), 195 (16), 105 (10), 43 (10).

**Analysis for C$_{30}$H$_{30}$MoO$_3$**

Calcd C 67.41 H 5.66 Mo 17.95%.

Found C 67.24 H 5.76 Mo 17.59%.

**Tris(but-3-en-2-one)molybdenum (8a)**

To a green suspension of 1.40 g (5 mmol) of bis($\eta^6$-toluene)molybdenum in 20 ml of n-hexane,
 freshly distilled but-3-en-2-one (1.75 g, 25 mmol) is added at room temperature with stirring. The colour of the reaction mixture immediately
changes to yellow-brown. Stirring is continued at
room temperature for 24 h, afterwards the volatile
components are removed under reduced pressure and the residue is extracted with three 20 ml portions of diethyl ether. After filtration and evaporation of the ether, the residue is washed once with 5 ml of cold n-pentane and then recrystallized from diethyl ether.

Yield: 1.05 g (3.4 mmol, 69%); m.p. 153–154 °C, other analytical data identical to those reported by King [4]: 13C NMR (CDCl3): δ 171.56 (s, 3 C, C=O), 86.62 (d, 3 C, =CH), 56.36 (t, 3 C, =CH2).

The crystal structure analysis of 6b [20, 21]

Crystals of 6b were obtained from a dichloromethane solution. Molecular formula C30H30O3W, molecular weight 622.4 g mol⁻¹, crystal colour orange-yellow, crystal size 0.28 x 0.35 x 0.35 mm, a = 15.724(3), b = 9.030(1), c = 17.690(4) A, β = 95.74(1)°, V = 2499.2 Å³, T = 293 K, dcal = 1.65 g cm⁻³, μ = 47.47 cm⁻¹, Z = 4, monoclinic, space group P21/c (No. 14). Enraf-Nonius CAD4 diffractometer, λ = 0.71069 A, scan mode ω-2θ, 5496 measured reflections (± h, k, l), [sin θ/λ]max 0.65 Å⁻¹, spherical absorption correction (min. transmission: 0.328; max.: 0.342), 5006 independent reflections, 4234 observed reflections [I > 2σ(I)] for 307 refined parameters, structure solved by heavy atom method, H atom positions calculated and fixed (UH = 0.05 Å²), residual electron density 1.37 e Å⁻³. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table IV.

The crystal structure analysis of 7b [20, 21]

Crystals were obtained from a tetrachloromethane solution of 7b. Molecular formula C30H30O3W, molecular weight 622.4 g mol⁻¹, crystal colour yellow, crystal size 0.28 x 0.35 x 0.35 mm, a = 17.616(2), b = 9.030(1), c = 17.690(4) A, β = 95.74(1)°, V = 5040.9 Å³, T = 293 K, dcal = 1.64 g cm⁻³, μ = 47.07 cm⁻¹, Z = 8, monoclinic, space group P21/c (No. 14). Enraf-Nonius CAD4 diffractometer, λ = 0.71069 A, scan mode ω-2θ, 5496 measured reflections (± h, k, l), [sin θ/λ]max 0.65 Å⁻¹, spherical absorption correction (min. transmission: 0.465; max.: 0.474), 3666 independent reflections, 2803 observed reflections [I ≥ 2σ(I)] for 283 refined parameters, structure solved by heavy atom method, W atom refined anisotropically, C and O atoms isotropic, H atom positions calculated and fixed (UH = 0.05 Å²), R = 0.041, Rw = 0.045 [w = 1/σ²(Fo)], residual electron density 0.67 e Å⁻³. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table V.

Reaction of tris(1-phenylprop-2-en-1-one)-molybdenum or -tungsten with H2

A solution of 1 mmol of the phenylpropenone complexes 5a or 5b in 50 ml of diethyl ether is placed in a glass vessel inserted into a 250 ml stainless steel autoclave. Under 10 MPa of hydrogen pressure the reaction mixture is then heated to 85 °C for 40 h. After cooling and removal of the excess hydrogen the grey suspension is filtered and the filtrate reduced in vacuo (3000 Pa). The residual oil was identified as 1-phenylpropan-1-one by comparison with an authentic sample.
<table>
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<tr>
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<tr>
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<tr>
<td>O4</td>
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<td>O5</td>
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<td>0.3157(4)</td>
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</table>

Table V. Atomic coordinates and equivalent isotropic thermal parameters (Å²) for 7b with standard deviations in parentheses.

Yield: 370 mg (2.76 mmol, 92%) from complex 5a (M = Mo); 300 mg (2.24 mmol, 74%) from complex 5b (M = W).

**Tris(1-cyclohexylprop-2-en-1-one)molybdenum (12)**

In a 100 ml stainless steel autoclave, a solution of 247 mg (0.5 mmol) of tris(1-phenylprop-2-en-1-one)molybdenum (5a) in 20 ml of diethyl ether is placed in an inserted glass vessel, 10 mg of platinum dioxide and 1.0 g of magnesium sulphate-monohydrate are added. After flushing with hydrogen at room temperature, hydrogen is introduced at a starting pressure of 6 MPa. The reaction mixture is magnetically stirred for 96 h at 35 °C. The remaining hydrogen pressure is removed and the pale-yellow reaction mixture filtered and reduced in vacuo. The oily residue is recrystallized from pentane between 20 °C and -78 °C. Pale-yellow needles of 12 are dried under high vacuum (10⁻² Pa).

Yield: 170 mg (0.33 mmol, 66%); m.p. 125-126 °C; 1H NMR (CD₃OH, δ 4.04 (m, 3H, =CH₂, α), 2.66 (m, 3H, =CH₂, β), 2.28 (m, 3H, =CH₂, β), 2.10-1.09 (m, 33 H, cyclohexyl); 13C NMR (all signals corresponding to three equivalent carbon atoms): δ 179.36 (s, C=O), 81.88 (d, =CH), 57.42 (t, =CH₂), 44.36 (d, cyclohexyl), 30.46 (t), 29.50 (t), 26.51 (t), 26.23 (t), 26.21 (t); IR (KBr): ν 2922 (s), 2853 (m), 1503 (w), 1475 (s), 1386 (m), 1351 (m), 1265 (t), 2.66 (m, 3H, =CH₂, β), 2.28 (m, 3H, =CH₂, β), 2.10-1.09 (m, 33 H, cyclohexyl); 13C NMR (all signals corresponding to three equivalent carbon atoms): δ 179.36 (s, C=O), 81.88 (d, =CH), 57.42 (t, =CH₂), 44.36 (d, cyclohexyl), 30.46 (t), 29.50 (t), 26.51 (t), 26.23 (t), 26.21 (t); IR (KBr): ν 2922 (s), 2853 (m), 1503 (w), 1475 (s), 1386 (m), 1351 (m), 1321 (w), 1169 (m), 950 (w), 893 (m), 720 (s) cm⁻¹; MS (EI): m/z (rel. int. [%]) 512 (M⁺, 10), 374 (M⁺-C₆H₁₄O, 100), 232 (20), 192 (19), 81 (20), 55 (40).

**Analysis for C₂₇H₄₂MoO₃**

Calcd C 63.52 H 8.29 Mo 18.79%.
Found C 63.37 H 8.97 Mo 18.83%.
According to the procedure for 12, complex 6b is employed as starting material. Reaction conditions: 8 MPa hydrogen pressure, 60 °C, 96 h.

Yield: 84%; m.p. 167–169 °C; \(^1\)H NMR (CDCl\(_3\), 400.134 MHz): \(\delta\) 2.77 (m, 3H, CH(cyclohex.)), 1.79 (s, 9H, CH\(_3\)), 1.87–1.05 (m, 30H, CH\(_2\)(cyclohex.)), 1.40 (d, 3H, =CH\(_2\), \(^2\)J\(_{HH}\) = 4.7 Hz), 0.99 (d, 3H, =CH\(_2\)); \(^{13}\)C NMR (100.614 MHz, all signals corresponding to three equivalent carbon atoms): \(\delta\) 167.48 (s, C=O), 91.34 (d, =CH), 64.11 (t, =CH\(_2\), \(^1\)J\(_{WC}\) = 35.2 Hz), 40.20 (d, CH(cyclohex.)), 30.42 (t), 26.90 (t), 26.57 (t), 26.43 (t), 25.64 (t), 16.97 (q, CH\(_3\)); IR (KBr): \(\nu\) 2922 (s), 2850 (m), 1500 (w), 1449 (s), 1376 (m), 1332 (w), 1089 (m), 869 (m), 691 (m), 680 (m) cm\(^{-1}\); MS (EI): \(m/z\) (rel. int. [%]) 640 (M\(^+\), 11), 488 (M\(^+\)–C\(_{10}\)H\(_{10}\)O, 100), 352 (30), 135 (38), 81 (52), 55 (58), 41 (58).

**Analysis for C\(_{50}\)H\(_{40}\)WO\(_3\)**
- Calcd C 56.25 H 7.55%.
- Found C 56.12 H 7.63%.

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**General procedure for the cyclotrimerization of 1-alkynes**

In an NMR tube, the metal complex (0.02 mmol) is added to a solution of 2.0 mmol of the 1-alkyne dissolved in 300 \(\mu\)l of C\(_6\)D\(_6\). The tube is then heated by immersion into an oil bath of constant temperature and the progress of the reaction monitored by \(^1\)H and \(^{13}\)C NMR. At the end of the reaction, products are also analyzed by GLC and isolated by chromatography on silica.

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[20] Structure determination on VAX 4000-300 computers. Computer programs (a–d) and supplementary data (e) used:
   a) data reduction: DATAP, P. Coppens, L. Leisewitz, D. Rabinovich, Acta Crystallogr. A 46, 467 (1990);
[21] Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 58745 and the journal citation.