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**THERMAL DECOMPOSITION OF (η -CYCLOPENTADIENYL)-
TRICARBONYL(σ -PHENYLETHYNYL)MOLYBDENUM AND THE
MOLECULAR STRUCTURE OF A MOLYBDENUM BINUCLEAR COMPLEX
WITH A BRIDGING 1,4-DIPHENYLBUTADIYNE LIGAND [(η -
 C_5H_5)(CO) $_2$ Mo] $_2$ (μ -1,2- η - $C_6H_5C\equiv C-C\equiv CC_6H_5$)**

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Summary

Thermolysis of $C_5H_5(CO)_3MoC\equiv CC_6H_5$ (I) in octane at 110–115°C results in the formation of [(η - C_5H_5)(CO) $_2$ Mo] $_2$ (μ -1,2- η - $C_6H_5C\equiv C-C\equiv CC_6H_5$) (II). The structure of II was determined by X-ray analysis. The reaction scheme is discussed.

Introduction

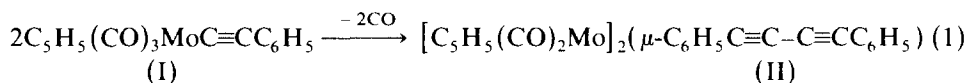
Thermal decomposition of the σ -1-alkynyl derivatives of transition metals is interesting because of its outcome and the mechanism. The presence of a non-coordinated triple bond makes oligomerization through the triple bond possible, as well as the formation of homometallic bi- and polynuclear complexes with a bridging σ , π -alkynyl ligand and metal-carbon σ -bond scission. Nevertheless, there are hardly any reports in the literature on the thermolysis of σ -1-alkynyl derivatives of transition metals. The present paper reports the thermal decomposition of $C_5H_5(CO)_3MoC\equiv CC_6H_5$ (I) [1], as well as the molecular structure of the product of this reaction (II).

Results and discussion

Heating I in the solid state at 118–120°C or in octane at 110–115°C followed by chromatographic separation yields a red crystalline complex of molecular formula $C_{15}H_{10}O_2Mo$ (II). The IR spectrum of II corresponds to the structure [$C_5H_5(CO)_2Mo$] $_2$ (μ -alkyne). For objective determination of the structure, this complex was subjected to X-ray analysis. It was found that II represents μ -(1,2- η -1,4-diphenylbutadiyne)bis[(η -cyclopentadienyl)dicarbonylmolybdenum], which contains

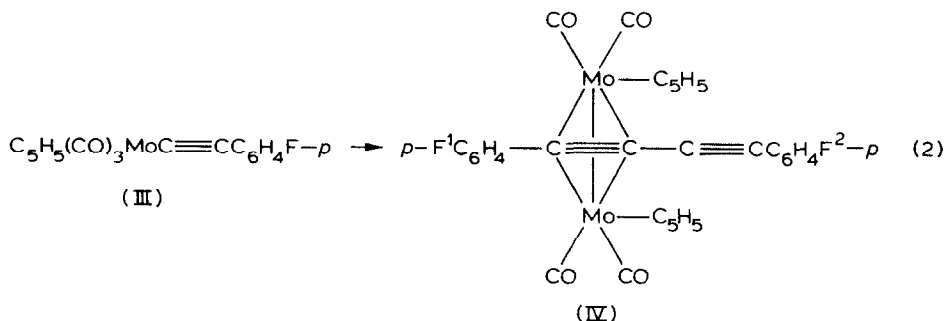
two $C_5H_5(CO)_2Mo$ fragments linked by a metal-metal bond, while the 1,4-diphenylbutadiyne molecule acts as a bridge, being bonded to each molybdenum atom by only one triple bond.

Thus, thermolysis of I can be described as follows:

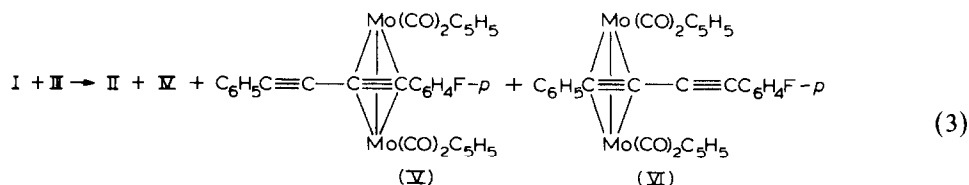


The yield of II does not exceed 17%. A special experiment proved that II decomposes under thermolysis conditions without the formation of any identifiable products. Simultaneously, during the process of reaction 1, a brown amorphous substance is formed together with II. According to the IR spectrum, this product, which appeared in trace amounts, possesses the $[C_5H_5(CO)_2Mo]_2(\mu\text{-alkyne})$ frame and its chromatographic mobility is lower than that of II. The compound was not studied further since it proved impossible to obtain crystals suitable for X-ray analysis.

Thermal decomposition of $C_5H_5(CO)_3MoC\equiv CC_6H_4F-p$ (III) * takes place under conditions similar to those of the thermolysis of I, although the yield of the main product (IV) is noticeably lower (5–7%) due to its increased instability with respect to thermolysis. The $^{19}F\{^1H\}$ NMR spectra contain two signals of F nuclei at +2.15 (F(1)) and -1.07 ppm (F(2)) **.



When heated together, I and III yield, in addition to II and IV, products of cross α,α -coupling of the σ -ethynyl groups V and VI:



* Complex III was synthesized with a 35% yield by treating $C_5H_5(CO)_3Mo^- K^+$ with $p-FC_6H_4C\equiv CBr$. This reaction, like other reactions of halogen substitution in 1-haloalkyne under the influence of metal-carbonyl anions, will be published elsewhere.

** In relation to the quasi-internal fluorobenzene standard in the same solvent.

In accordance with the above, the $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of the product of reaction 3 contain signals of IV as well as signals of F nuclei at +2.25 and -0.84 ppm which are due to V and VI, respectively.

In discussing the thermolysis scheme it should be borne in mind that no phenylacetylene or 1,4-diphenylbutadiyne was found in the reaction mixture. In most cases, during thermolysis of transition metal σ -organic derivatives, the M-R bond breaks leading to RH, R(-H) and R-R, the ratio of the products of disproportionation and dimerization being strongly dependent on the nature of R and the metal. The occurrence of R-R as the main product of heat decomposition is usually explained by either homolytic splitting of the M-R bond [2] or by the binuclear elimination mechanism [2,3]. It is a characteristic feature of the thermolysis of I that the product of dimerization, 1,4-diphenylbutadiyne, does not leave the coordination sphere of the Mo atom but becomes a bridging ligand and leads to the formation of II.

It is evident that the process of formation of II from I incorporates several stages. One of the possible schemes involves initial homolytic splitting of the Mo-C bond with the formation of two radicals, $\text{C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot$ (VII) and $\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot$ (VIII); dissociation of VII to CO and $\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}\cdot$ (IX); and dimerization of radicals IX and VIII with respective formation of $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}]_2$ (X) and 1,4-diphenylbutadiyne; finally, the reaction of X with 1,4-diphenylbutadiyne results in the formation of II. Despite the fact that the transformation VII \rightarrow IX \rightarrow X during photolysis or thermolysis of $[\text{C}_5\text{H}_5(\text{CO})_3\text{Mo}]_2$ has been described [4,5], and the reaction of X with 1,4-diphenylbutadiyne has a direct analogue in the literature [5,6], a series of our experimental observations contradicts this scheme. For instance, special experiments proved that under conditions of process 1, i.e. in octane at 120°C, X reacts with 1,4-diphenylbutadiyne resulting in only traces of II. As already mentioned, the products of $\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot$ transformation, i.e. phenylacetylene and 1,4-diphenylbutadiyne, are absent from the reaction mixture. During thermolysis of I in toluene, the yield of II remains practically the same; methyl-substituted tolans were not identified, although it is known [7,8] that $\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot$ reacts with toluene according to the radical substitution reaction. And finally, during photolysis of I which promotes homolysis of the molybdenum-phenylethynyl bond, $\text{C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot$ was not detected with a spin trap*.

That is why the alternative scheme is more probable. It includes the dissociation of the CO group with formation of the intermediate XI of unsaturated coordination, its dimerization to structures of type XII or XIII, and subsequent α,α -combination of the phenylethynyl groups and formation of Mo-Mo bonds with simultaneous change in the character of the coordination interaction, which leads to the formation of II. This scheme is compatible with the results of the crossover experiment (eq. 3). Indirectly, scheme 1 is confirmed by the formation of the previously described [10] phosphine-substituted derivative (XIV), if thermolysis of I is conducted in the presence of triphenylphosphine. Under these conditions, practically no II is formed at all, while the yield of XIV amounts to 10-20%, which is due to the instability of

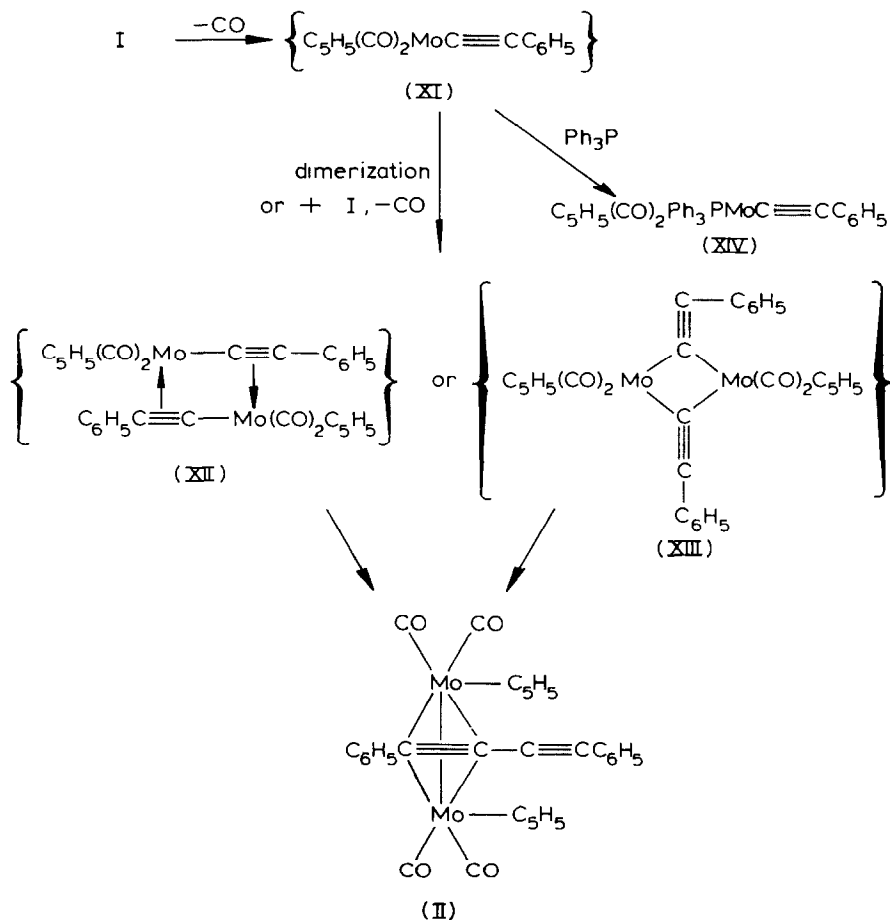
* No signals of the $[\text{C}_5\text{H}_5(\text{CO})_3\text{Mo}-\text{N}(\text{O})\text{C}_6\text{H}(\text{CH}_3)_4]\cdot$ radical, whose ESR spectrum was described in ref. 9, were registered under UV (300, 366 nm) irradiation of I in benzene in an ESR RE-1306 spectrometer cell in the presence of nitrosodurole.

XIV during thermolysis, as proved in a special experiment. It is noteworthy that the reaction of I with triphenylphosphine to give XIV occurs in precisely the same temperature range as the thermolysis of I itself.

During the study of thermally induced reactions of I, it was difficult to establish the entire range of products, since complexes II and XIV decompose partially under the conditions described, while organic products probably undergo polymerization or oligomerization. This makes a final conclusion regarding reaction scheme 1 difficult at the moment.

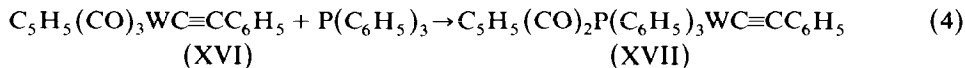
The analogous σ -phenylethynyl derivatives $C_5H_5(CO)_3MC\equiv CC_6H_5$ (XV, M = Cr; XVI, M = W) decompose in approximately the same temperature range as I. When XV is heated in the solid state or in octane at 100°C, trace amounts of a complex appear. According to the IR spectrum, it has the structure $[C_5H_5(CO)_2Cr]_2-(C_6H_5C\equiv C-C\equiv CC_6H_5)$. It was not characterized fully because it decomposes quickly during thermolysis.

When the tungsten compound XVI is heated in octane at 110°C or in the solid



SCHEME 1

state at 130–135°C, unidentified decomposition products form together with trace amounts of $[\text{C}_5\text{H}_5(\text{CO})_3\text{W}]_2$. Heating XVI with triphenylphosphine in octane at 150°C leads to a triphenylphosphine complex (XVII).



Molecular structure of II

The geometry of the molecule II (Fig. 1 and Table 1) is very similar to the previously described structures of type $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}]_2(\mu\text{-RC}\equiv\text{CR})$ [6] (XVIII, R = H; XIX, R = C_2H_5 ; XX, R = C_6H_5), which are characterized by non-equivalence of $\text{CpMo}(\text{CO})_2$ structural units because one of the carbonyl groups is semi-bridging.

The last feature results in shortening of the $\text{Mo}\dots\text{C}(\text{O})$ distance to the second metal atom. Thus, in molecule II a shortened $\text{Mo}(1)\dots\text{C}(3)$ contact, 2.909(3) Å, is observed, which is comparable to those found in XVIII (2.902 Å), XIX (2.826 Å) and XX (2.871 Å). This is responsible for significant bending of the metal-carbonyl group—the $\text{Mo}(2)\text{C}(3)\text{O}(3)$ bond angle is $169.2(3)^\circ$ (168.5° in XVIII, 168.1° in XIX and 168.6° in XX)—while other $\text{Mo}-\text{C}-\text{O}$ groups are essentially linear (mean value of the MoCO angle is 177.5°). According to [6], the structural non-equivalence of the

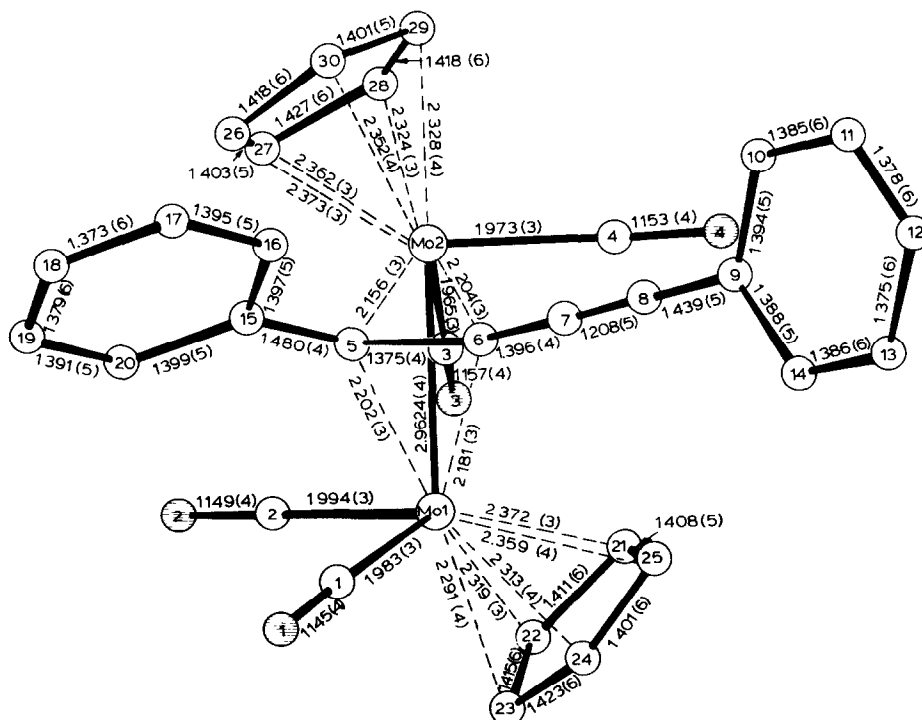


Fig. 1. Molecular geometry of the binuclear complex $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}]_2(\mu\text{-1,2-}\eta\text{-C}_6\text{H}_5\text{C}\equiv\text{C}-\text{C}\equiv\text{CC}_6\text{H}_5)$ (II).

two molecule halves in the series of compounds $[\text{CpMo}(\text{CO})_2]_2$ (μ -alkyne) is governed by the general steric strain of these molecules, which is due to the presence of bulky cyclopentadienyl and μ -alkyne ligands. However, a recent X-ray study of $[\text{CpMo}(\text{CO})_2]_2(\mu\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ (XXI) [11] showed that all the carbonyl ligands in this complex are equivalent and that the molecule has non-crystallographic C_2 symmetry (the two-fold axis passes through the middle of the Mo–Mo and $\text{C}\equiv\text{C}$ bonds). Nevertheless, the IR spectra of XXI in solutions [11] exhibit bands corresponding to isomers with semi-bridging carbonyl groups, i.e. the difference in the energies of isomers with terminal and semi-bridging carbonyl ligands seems to be small, and the “freezing” of a particular isomer in the crystal is evidently governed by packing forces.

The central fragment C(15)C(5)C(6)C(7)C(8)C(9) of the bridging diacetylene ligand in II is almost planar (Table 2), but the C(9)...C(14) and C(15)...C(20)Ph rings are turned by 74.2 and 22.7°, respectively, relative to this plane. The coordinated C(5) \equiv C(6) triple bond is perpendicular to the Mo(1)–Mo(2) bond (92.1°) and, as usual, is considerably elongated (to 1.375(4) Å) compared to acetylene (1.205 Å [12]) as a result of back-donation from non-bonding metal orbitals to the π^* -orbitals of the acetylene ligand. The length of the coordinated bond not only exceeds the standard C=C double-bond length (1.333 Å [12]), but is also significantly larger as compared with the corresponding bond lengths in the structures XVIII (1.337 Å), XIX (1.335 Å), XX (1.329 Å) and XXI (1.358 Å), although it is still within the range of bond lengths observed for μ_2 -alkyne ligands [13]. In addition, the C(5) \equiv C(6) triple bond is slightly twisted (torsion angle C(15)–C(5)–C(6)–C(7) is 5.0(5)°. Table 3), which is most probably due to steric hindrance between the ligands.

Another characteristic feature of π -acetylene complexes of transition metals is the considerable distortion of the linear configuration of the coordinated acetylene ligand towards a *cis*-stilbene structure, with the substituents bent away from the metal atom. In fact, the bond angles C(6)C(5)C(15), 131.8(3), and C(5)C(6)C(7), 136.5(3)°, differ from the ideal value (180°) by ca. 45° and are comparable to the R–C \equiv C angles in the molecules XVIII (138°), XIX (134.2°), XX (134.6°) and XXI

TABLE 1
BOND ANGLES ω (degrees) FOR II

Angle	ω	Angle	ω	Angle	ω
Mo(2)Mo(1)C(1)	123.50(9)	C(8)C(9)C(10)	120.6(3)	C(17)C(18)C(19)	119.4(4)
Mo(2)Mo(1)C(2)	81.64(9)	C(8)C(9)C(14)	120.7(3)	C(18)C(19)C(20)	120.7(4)
C(1)Mo(1)C(2)	85.5(1)	C(10)C(9)C(14)m	118.6(3)	C(15)C(20)C(19)	120.4(3)
Mo(1)Mo(2)C(3)	68.99(9)	C(9)C(10)C(11)	120.1(3)	C(22)C(21)C(25)	108.0(3)
Mo(1)Mo(2)C(4)	89.03(9)	C(10)C(11)C(12)	120.4(4)	C(21)C(22)C(23)	107.8(3)
C(3)Mo(2)C(4)	89.5(1)	C(11)C(12)C(13)	120.2(4)	C(22)C(23)C(24)	107.9(3)
Mo(1)C(1)O(1)	176.3(3)	C(12)C(13)C(14)	119.7(4)	C(23)C(24)C(25)	107.6(3)
Mo(1)C(2)O(2)	178.9(3)	C(9)C(14)C(13)	121.0(3)	C(21)C(25)C(24)	108.7(3)
Mo(2)C(3)O(3)	169.2(3)	C(5)C(15)C(16)	118.9(3)	C(27)C(26)C(30)	108.2(3)
Mo(2)C(4)O(4)	177.2(3)	C(5)C(15)C(20)	122.8(3)	C(26)C(27)C(28)	107.9(3)
C(6)C(5)C(15)	131.8(3)	C(16)C(15)C(20)	118.3(3)	C(27)C(28)C(29)	107.4(3)
C(5)C(6)C(7)	136.5(3)	C(15)C(16)C(17)	120.3(3)	C(28)C(29)C(30)	108.3(3)
C(6)C(7)C(8)	175.5(3)	C(16)C(17)C(18)	120.9(4)	C(26)C(30)C(29)	108.1(3)
C(7)C(8)C(9)	177.5(3)				

(137.3°). According to quantum chemical calculations [14], the degree of bending of the acetylene ligand on coordination is totally governed by the π -component of the metal \rightarrow alkyne bond (dative interaction); therefore the considerable deviation of substituents at the triple bond in II and XVIII–XXI indicates a strong contribution of just the π -component.

TABLE 2
PLANAR MOLECULAR FRAGMENTS OF II

(a) Atomic displacement from mean planes (Å)					
	Δ	Δ/σ		Δ	Δ/σ
<i>Plane 1</i>			<i>Plane 4</i>		
C(15)	-0.006	1.73	C(21)	0.004	1.32
C(5)	0.013	4.22	C(22)	-0.005	1.65
C(6)	-0.015	4.95	C(23)	0.004	1.26
C(7)	0.014	4.51	C(24)	-0.002	0.43
C(8)	-0.011	3.37	C(25)	-0.002	0.53
C(9)	0.004	1.21			
<i>Plane 2</i>			<i>Plane 5</i>		
C(9)	0.005	1.66	C(26)	0.001	0.42
C(10)	-0.006	1.57	C(27)	-0.004	1.13
C(11)	0.001	0.12	C(28)	0.005	1.42
C(12)	0.005	1.22	C(29)	-0.004	1.14
C(13)	-0.004	0.89	C(30)	0.002	0.45
C(14)	-0.003	0.72			
<i>Plane 3</i>			<i>Plane 6</i>		
C(15)	0.004	1.23	Mo(1)	0	0
C(16)	-0.001	0.33	C(5)	0	0
C(17)	-0.004	0.85	Mo(2)	0	0
C(18)	0.003	0.81	<i>Plane 7</i>		
C(919)	0.002	0.38	Mo(1)	0	0
C(20)	-0.005	1.34	C(6)	0	0
			Mo(2)	0	0

(b) Equation of planes $Ax + By + Cz - D = 0$

Plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
1	-0.6774	0.6281	-0.3829	0.1057
2	0.5848	-0.2704	-0.7648	-3.0036
3	-0.8619	0.2827	-0.4209	-1.1317
4	-0.1583	0.0798	-0.9842	0.1675
5	-0.6312	0.2101	-0.7466	-5.4602
6	-0.4329	-0.8035	-0.4086	-4.1635
7	0.1717	-0.4323	-0.8852	-3.6252

(c) Relevant dihedral angles τ (degrees)

Plane	τ	Plane	τ
1-2	74.2	4-5	148.4
1-3	22.7	6-7	50.6
2-3	105.0		

TABLE 3
RELEVANT TORSION ANGLES φ (°) IN II

Angle	φ	Angle	φ
C(15)–C(5)–C(6)–C(7)	5.0(5)	C(2)–Mo(1)–Mo(2)–C(4)	–156.0
C(5)–C(6)–C(7)–C(8)	–150(4)	Q(1)–Mo(1)–Mo(2)–Q(2) ^a	154.0
C(6)–C(7)–C(8)–C(9)	–167(8)	Q(1)–Mo(1)–Mo(2)–C(3)	56.8
C(1)–Mo(1)–Mo(2)–C(3)	–145.1(3)	Q(1)–Mo(1)–Mo(2)–C(4)	–33.0
C(1)–Mo(1)–Mo(2)–C(4)	125.1(2)	Q(2)–Mo(2)–Mo(1)–C(1)	–47.9
C(2)–Mo(1)–Mo(2)–C(3)	–66.2(2)	Q(2)–Mo(2)–Mo(1)–C(2)	31.0

^a Q(1) and Q(2) are centroids of the cyclopentadienyl rings C(21)–C(25) and C(26)–C(30), respectively.

Another characteristic feature of the π -acetylene complexes is the decrease of interatomic M–C(alkyne) distances relative to the sums of covalent radii or the lengths of the corresponding metal–carbon σ -bonds. Thus, the average Mo–C (acetylene) distances in the structures considered (2.174(3) (II), 2.172 (XVIII), 2.203 (XIX), 2.182 (XX) and 2.228 Å (XXI)) are considerably shorter than the sum of radii of Mo (1.58 Å [15]) and C(*sp*) (0.70 Å)*, which again confirms a considerable $d_{\pi} \rightarrow \pi^*$ metal–alkyne interaction.

Concerning the other geometrical parameters of the diacetylene ligand, the following items seem worth mentioning: (1) the length of the non-coordinated triple bond C(7)≡C(8), 1.208(5) Å, corresponds to the standard value (1.205 Å [12]); (2) the linearity of the C(6)–C(7)–C(8)–C(9) fragment is retained, the bond angles C(6)C(7)C(8) and C(7)C(8)C(9) being 175.5(3) and 177.5(3)°, respectively (cf. also the torsion angles in Table 3); (3) the C(8)–C(9) distance of 1.439(5) Å is close to the expected value of 1.426 Å for bonds of the C(*sp*)–C(*sp*²) type [12], while the C(5)–C(15) bond length of 1.480 Å is very close to the value of 1.476 Å which is used for C(*sp*²)–C(*sp*²) bonds; (4) the C(6)–C(7) bond length of 1.396 Å lies between the standard values of C(*sp*)–C(*sp*) (1.376 Å [12]) and C(*sp*)–C(*sp*²) bond lengths.

The planar cyclopentadienyl rings, which have an average C–C bond length of 1.412(9) Å, are in the *trans*-position with respect to each other (pseudo-torsion angle Q(1)–Mo–Mo–Q(2) (Q(1) and Q(2) are Cp ring centroids) is 154.0°; Table 4). As is typical for seven-coordinated CpMoL₃R complexes (L and R are two- and one-electron donors, respectively), the cyclopentadienyl rings are tilted. This is evident from the non-equivalence of the Mo–C(Cp) distances, which vary in the range of 2.291–2.372 Å. At the same time, the average distance of 2.399(28) Å is in good agreement with the corresponding values in the molecules of XVIII (2.340 Å), XIX (2.344 Å) and XX (2.332 Å), as well as in other molybdenum η^5 -cyclopentadienyl complexes.

Comparison of the metal–metal bond lengths in structures II and XVIII–XXI reveals an interesting feature: in the molecules of II, XX and XXI with bulky substituents at the acetylene carbon atoms of the bridging ligand, the Mo–Mo bonds

* In this case, it seems more appropriate to take the value 0.74 Å (C(*sp*²)) for the C atom radius in view of the effective orbital rehybridization of the C atom in the acetylene ligand on coordination with the metal, which is demonstrated by both stretching of the triple C≡C bonds, and decrease of the R–C≡C bond angles to values that are close to the ideal angle (120°) for *sp*² hybridization.

TABLE 4
 ATOMIC POSITIONAL ($\times 10^4$; for $\text{Mo} \times 10^5$) AND THERMAL PARAMETERS (\AA^2) IN THE FORM
 $B_{\text{eq}} = 1/3 \sum \sum B_{ij} a_i^* a_j^* (a_i a_j)$ FOR II

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Mo(1)	2655(3)	16622(1)	18080(2)	1.04(1)	C(13)	-5098(5)	-813(2)	1048(4)	2.51(10)
Mo(2)	27282(3)	9419(1)	28504(2)	1.03(1)	C(14)	-4091(4)	-374(2)	1276(3)	2.03(9)
O(1)	-2599(3)	2131(1)	3044(2)	2.45(7)	C(15)	-100(4)	1297(1)	4553(3)	1.30(7)
O(2)	2223(3)	2578(1)	3108(2)	1.99(6)	C(16)	-821(4)	847(2)	5053(3)	1.89(9)
O(3)	4360(3)	1722(1)	1193(2)	2.04(6)	C(17)	-1426(5)	901(2)	6111(3)	2.57(10)
O(4)	2041(3)	71(1)	960(2)	2.46(7)	C(18)	-1329(5)	1395(2)	6677(3)	2.51(10)
C(1)	-1550(4)	1943(1)	2616(3)	1.44(8)	C(19)	-613(5)	1842(2)	6195(3)	2.21(9)
C(2)	1494(4)	2245(1)	2639(3)	1.37(7)	C(20)	7(4)	1797(1)	5144(3)	1.65(8)
C(3)	3614(4)	1451(2)	1764(3)	1.57(8)	C(21)	1007(4)	1441(2)	-26(3)	1.95(9)
C(4)	2325(4)	398(1)	1641(3)	1.55(8)	C(22)	905(5)	2022(2)	90(3)	2.19(9)
C(5)	510(3)	1227(1)	3423(3)	1.20(7)	C(23)	-672(5)	2155(2)	286(3)	2.21(9)
C(6)	172(3)	848(1)	2591(3)	1.19(7)	C(24)	-1535(4)	1651(2)	308(3)	2.27(9)
C(7)	-887(4)	413(1)	2413(3)	1.25(7)	C(25)	-493(4)	1217(2)	116(3)	2.10(9)
C(8)	-1729(4)	20(1)	2216(3)	1.35(7)	C(26)	3591(4)	1088(2)	4739(3)	1.82(8)
C(10)	-2520(5)	-948(1)	2507(3)	1.87(8)	C(28)	5287(4)	755(2)	3474(3)	2.24(9)
C(11)	-3526(5)	-1387(2)	2271(3)	2.44(10)	C(29)	4338(4)	310(2)	3818(3)	2.28(9)
C(12)	-4806(5)	-1319(2)	1543(3)	2.45(10)	C(30)	3292(4)	514(2)	4588(3)	2.09(9)

are somewhat shorter (2.9624(4) (II), 2.956 (XX) and 2.952 Å (XXI)) than those in structures XVIII (2.980 Å) and XIX (2.977 Å) where more compact groups are bonded to the coordinated C atoms. It seems that the difference in the Mo–Mo bond lengths is governed by their different electron interactions, in addition to the steric influence of the terminal substituents in the bridging acetylene ligand.

Experimental

All manipulations except preparative GLC were conducted in an argon atmosphere. Silica gel (Chemapol, CSSR, L 100/160 μ) was used for chromatography. GLC analysis was conducted with an LHM 8D chromatograph. IR spectra were taken with a UR-20 spectrometer (Carl Zeiss, G.D.R.); NMR spectra with a Jeol FX 100. The starting σ -phenylethynyl complexes $C_5H_5(CO)_3MC\equiv CC_6H_5$ (M = Cr, Mo, W) were synthesized according to previously described methods [1].

1. Thermolysis of $C_5H_5(CO)_3MoC\equiv CC_6H_5$ (I) in octane

A solution of 1 g of I in 30 ml of octane was heated at 110–115°C for 2 h. The mixture turned dark red with apparent gas evolution. After removal of the solvent in vacuo, the residue was subjected to chromatography on silica gel plates, using a mixture of petroleum ether and benzene (1/1) as the eluent. Two coloured zones appeared: dark red, and brown, the latter being less mobile. The contents of the colourless zone that preceded the dark red one did not include phenylacetylene or 1,4-diphenylbutadiyne, which was proved by GLC. After extraction of the dark-red band with methylene chloride, 0.15 g of II was obtained (17%). M.p. 158°C (hexane). $\nu(CO)(\text{cyclohexane})$ 1860, 1960, 2000 cm^{-1} . Found: C, 54.87; H, 3.33; Mo, 30.86. $C_{30}H_{20}Mo_2O_4$ calcd.: C, 56.62; H, 3.17; Mo, 30.16%. In the mass spectrum of II, in accordance with isotope molybdenum distribution, groups of peaks of the following ions were observed: $[P-4CO]^+$, $[Cp_2Mo_2(CO)_4]^+$, $[Cp(CO)_3Mo]^+$, $[Cp(CO)_2Mo]^+$, $[(PhC\equiv C)_2]^+$, $[CpMo]^+$, $[Mo]^+$. 1H NMR (δ , $CDCl_3$): 5.23 (singlet, C_5H_5), 7.09–7.61 (multiplet, C_6H_5). ^{13}C NMR (δ , CD_2Cl_2): 93.56 (C_5H_5), 91.4 and 94.4 ($C\equiv C$ coord.), 124.8, 126.2, 127.5, 128.8, 128.9, 131.76 (C_6H_5 and $C\equiv C$ non-coord.), 146.6 (*C(ips)*, non-coord.), 228.4 and 230.3 (CO).

Following extraction, the brown band yielded 0.005 g of amorphous crystals. $\nu(CO)(\text{cyclohexane})$ 1860, 1960, 2005 cm^{-1} . The structure of the substance was not determined.

2. Thermolysis of I in the solid state

Heating 0.1 g of I at 118–120°C for 2 h and TLC separation of the dark-red residue as described in experiment (1) resulted in 0.01 g of II together with traces of $[C_5H_5(CO)_3Mo]_2$.

3. Thermolysis of $C_5H_5(CO)_3MoC\equiv CC_6H_4F-p$ (III)

A solution of 0.5 g of III in 10 ml of octane was heated at 120°C for 30 min. The colour of the solution changed from yellow to dark red. The reaction mixture was treated as in experiment 1. From the more mobile red band, 0.03 g of complex IV was obtained (6%), m.p. 159–161°C. $\nu(CO)(\text{cyclohexane})$ 1860, 1960, 2000 cm^{-1} . The contents of the less mobile brown band were discarded.

4. Thermolysis of I and III

A solution of 0.3 g of I and 0.3 g of III in 50 ml of octane was heated for 30 min. After removal of octane in vacuo and chromatography conducted as in experiment 1, 0.07 g of red crystals were obtained which, according to IR and NMR data, proved to be a mixture of II and IV–VI.

5. Heating I with triphenylphosphine

A mixture of 0.28 g (0.8 mmol) of I and 0.41 g (1.5 mmol) Ph_3P was heated in 10 ml of octane at 120°C for 2.5 h until I had disappeared completely (IR spectrum control). After the solvent had been removed in vacuo, the residue was subjected to chromatography on silica gel plates in benzene. The yellow band yielded 0.05 g (10%) of $\text{C}_5\text{H}_5(\text{CO})_2\text{Ph}_3\text{PMoC}\equiv\text{CC}_6\text{H}_5$ (XIV). The m.p. and IR spectrum of XIV were identical to those previously described in [10].

6. Heating $\text{C}_5\text{H}_5(\text{CO})_3\text{WC}\equiv\text{CC}_6\text{H}_5$ (XV) with triphenylphosphine

A mixture of 0.1 g (0.2 mmol) of XV and 0.08 g (0.03 mmol) of triphenylphosphine in 5 ml of nonane was refluxed for 4 h. The solution turned black, and TLC revealed that starting XV was absent from the mixture. After treatment of the reaction mixture as in the previous experiment, 0.05 g (33%) of yellow crystals, $\text{C}_5\text{H}_5(\text{CO})_2\text{Ph}_3\text{PWC}\equiv\text{CC}_6\text{H}_5$ (XVII), were obtained. M.p. $206\text{--}207^\circ\text{C}$. $\nu(\text{CO})$ (CHCl_3) $1874, 1959\text{ cm}^{-1}$. Found: C, 62.25; H, 3.77; $\text{C}_{33}\text{H}_{25}\text{O}_2\text{PW}$ calcd.: C, 59.29; H, 3.77%. $^1\text{H NMR}$ (δ , CDCl_3): 5.415, 5.413 (doublet, C_5H_5), 7.25–7.60 (multiplet, C_6H_5).

An X-ray study was carried out with a Syntex P2_1 automatic diffractometer ($\lambda\text{Mo-K}_\alpha$, graphite monochromator) at -120°C .

Crystals of I are monoclinic, a 8.545(2), b 24.131(9), c 11.969(3) Å, β $92.51(2)^\circ$, V $2466(1)\text{ Å}^3$, $d_{\text{calcd.}}$ 1.71 g/cm^3 , $Z = 4$, space group $\text{P2}_1/n$, $\mu(\lambda\text{Mo-K}_\alpha)$ 10.37 cm^{-1} .

The intensities of 4888 independent reflections were measured by a $\theta/2\theta$ scan in the $2 \leq 2\theta \leq 52^\circ$ range; 3951 reflections with $I \geq 3\sigma$ were used in the calculations. Absorption correction was neglected. The structure was solved by the usual heavy atom method and refined to $R = 0.029$, $R_w = 0.042$ by the least-squares method in a full-matrix anisotropic approximation (isotropic for H atoms whose positions were calculated geometrically). The coordinates and temperature factors of non-hydrogen atoms are given in Table 4.

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