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Two Different Crystal and Molecular Structures for Dicarbonyl(η^2-*cis*-cyclooctene)[η^6-1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)-benzene]molybdenum(0): a Highly Crowded but Surprisingly Stable Molecule

John C. Barnes[1], **Geoffrey Hunter**[1,*], **Walter Keller**[2], **John D. Paton**[1], and **Walter Weissensteiner**[3,*]

[1] Department of Chemistry, The University, Dundee, DD1 4HN
[2] Institut für Physikalische Chemie, Universität Graz, A-8010 Graz, Austria
[3] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. Two crystal and molecular structures have been determined for the sterically very crowded molecule dicarbonyl(η^2-*cis*-cyclooctene)[η^6-1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)-benzene]-molybdenum(0), **3a** and **3b**. In structure **3a** the crystals are monoclinic, space group $P2_1/n$, whereas in **3b** they are orthorhombic, space group $P2_12_12_1$. In **3a** the carbon-carbon double bond of the *cis*-cyclooctene moiety is almost parallel to the benzene ring plane; in **3b** it is inclined at an angle of nearly 15°. In both **3a** and **3b** the co-ordinated *cis*-cyclooctene and arene moieties adopt conformations which are very similar to those calculated to be the ground states of the free molecules.

Keywords. X-ray diffraction; Conformational analysis, *Cis*-cyclooctene-arene-metal carbonyls.

Zwei unterschiedliche Kristall- und Molekülstrukturen von Dicarbonyl (η^2-*cis*-cycloocten)[η^6-1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)-benzol]molybdän(0): einem hochgespannten aber überraschend stabilen Molekül

Zusammenfassung. Von dem sterisch sehr gespannten Molekül Dicarbonyl(η^2-*cis*-cycloocten)[η^6-1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)-benzol]molybdän(0) wurden zwei unterschiedliche Kristall- und Molekülstrukturen **3a** und **3b** ermittelt. Die Kristalle von **3a** sind monoklin (Raumgruppe $P2_1/n$), jene von **3b** orthorhombisch (Raumgruppe $P2_12_12_1$). In **3a** ist die Kohlenstoff-Kohlenstoff Doppelbindung der *cis*-Cycloocteneinheit nahezu parallel zum Benzolring angeordnet; in **3b** ist sie um etwa 15° gekippt. Die Konformationen des koordinierten *cis*-Cycloocten sowie des Arens sind sehr ähnlich jenen Grundzustandsstrukturen, die für die nichtkoordinierten Moleküle berechnet wurden.

Introduction

It is considered that both hydrogenation and metal complexation of *trans*-cyclooctene are favoured processes which lead to substantial relief of ring strain, whereas the opposite situation applies with its *cis* isomer, for which they should actually involve small increases in strain energy [1 – 3]. Olefins, such as *cis*-cyclooctene, with less steric energy than the corresponding hydrocarbon have been called "hyperstable" or "hyperenergetic" molecules [4]. Thus, although *cis*-cyclooctene complexes are frequently prepared as intermediates in the ultimate substitution of a metal-bound carbonyl moiety by another ligand [5], they are themselves very air-sensitive and seldom isolated [6].Indeed X-ray crystallographic studies of only four compounds in which *cis*-cyclooctene is complexed to any metal have been previously reported: acetylacetonato(η^2-*cis*-cyclooctene)(η^2-hexafluorobut-2-yne)rhodium(I) [7]; bis(η^2-*cis*-cyclooctene)(μ-dichloro)bis[bis(trimethylsilylmethyl)-phosphine]dirhodium(I) [8]; chloro-(η^2-*cis*-cyclooctene)gold(I) [9]; bis(η^2-*cis*-cyclooctene)-copper(I)trifluoromethanesulphonate [10]. As (arene)M(CO)$_2$(alkene) (M = Cr, Mo) complexes also tend to be very unstable and air-sensitive [11] it was with surprise that from the products of the photolysis of *cis*-cyclooctene with the sterically very crowded molecule tricarbonyl[η^6-1,3,5-triethyl-2,4,6-*tris*(trimethylsilylmethyl)benzene]molybdenum(0), (**2**), we isolated the stable compound dicarbonyl(η^2-*cis*-cyclooctene)[η^6-1,3,5-triethyl-2,4,6-*tris*(trimethylsilylmethyl)benzene]-molybdenum(0), (**3**), in not just one, but two different crystal habits with markedly different orientations of the *cis*-cyclooctene carbon-carbon double bond relative to the ring plane of the co-ordinated arene. Moreover, in both cases, with the exception of a slight lengthening of the double bond of the *cis*-cyclooctene moiety, the overall conformation, bond lengths, angles and torsion angles are remarkably similar to those previously calculated for the free *cis*-cyclootene molecule [1, 2].

Results and Discussion

Molecules **1**, **2**, and **3** were synthesised as part of a major, ongoing program to study the conformational properties and internal mobilities of sterically crowded arenes and of their metal complexes [12]. Force field calculations [13] for 1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene, **1**, reveal that attractive steric interactions should result in a ground state conformation in which the three trimethylsilymethyl groups all project from the same side of the benzene ring plane. For one such group to project from the opposite side to the other two invokes such a large energy penalty that other than negligible populations of conformations with such an arrangement can be discounted. As might therefore be anticipated the ground state conformation of **1** has all three ethyl groups projecting from the opposite side of the benzene ring plane to the bulky trimethylsilylmethyl groups. However, the conformation with one ethyl group projecting from the same benzene ring face as the trimethylsilylmethyl groups is relatively low-lying at 22.1 kJ mol^{-1} above the ground state conformation and, although negligibly populated in the free arene, is a potential candidate to become the ground state conformation when (**1**) is hexa-hapto co-ordinated to a C$_s$ symmetrical metal-tripod moiety with at least one sterically-demanding ligand. Just such a situation has been observed to occur with hexaethylbenzene whose ground state conformation may change on complexation as a result of steric interaction with other ligands substituting the metal [12, 14].

The other conformations of **1**, with two and three ethyl groups projecting from the same face as the trimethylsilylmethyl groups, lie respectively at 44.2 and

71.1 kJ mol^{-1} above the ground state energy calculated for the molecule and must therefore be considered inaccessible even with the arene bound to a sterically very demanding moiety. The 90.56 MHz ^{13}C-{^{1}H}NMR spectrum of **1** in CD_2Cl_2 solution is unchanged even at 148 K and is entirely consistent with the conclusion drawn from the force field calculations that the ground state conformation for this molecule has three equivalent trimethylsilylmethyl groups and three equivalent ethyl groups.

The two benzene ring faces of **1** are, of course, inequivalent and that from which the trimethylsilymethyl groups project is inaccessible to a potentially co-

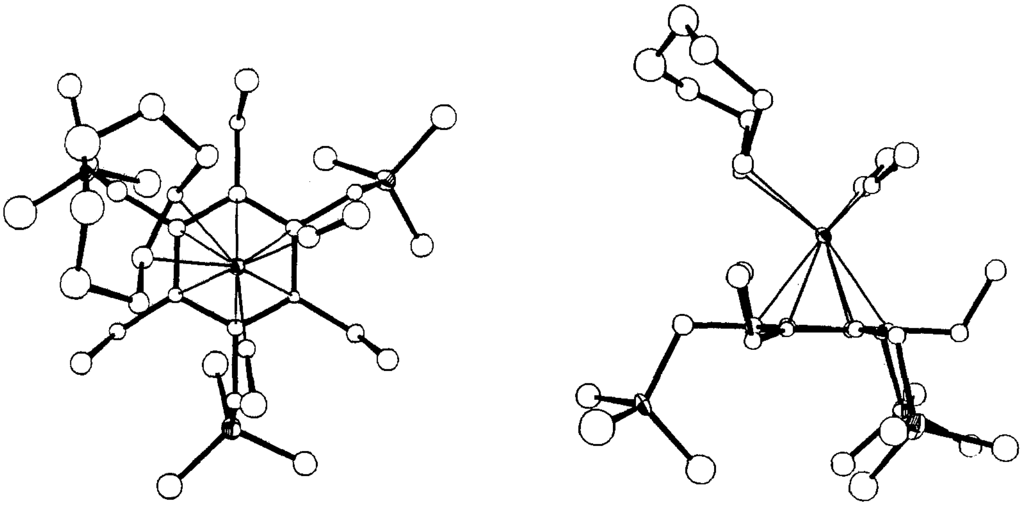


Fig. 1(i) **Fig. 1(ii)**

Fig. 1. ORTEP [19] drawing of the asymmetric unit in the crystal structure of **3a** from data collected at −177°C, (i) viewed perpenticular to the arene ring plane, (ii) parallel to the benzene ring. Non-hydrogen atoms were drawn at 50% probability level

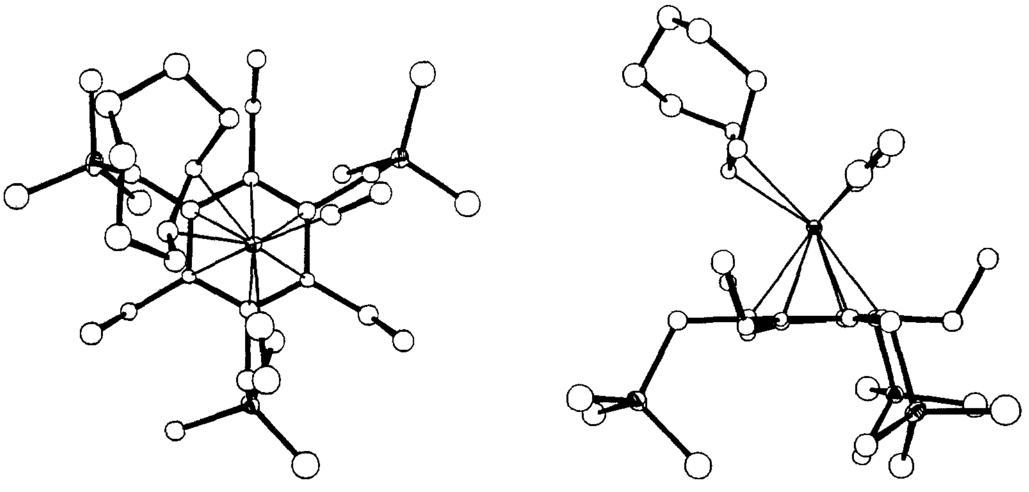


Fig. 1(i) **Fig. (ii)**

Fig. 2. As Fig. 1 for **3b** from data collected at −175°C

ordinating metal tricarbonyl fragment. The other face, from which project the ethyl groups should present similar steric hinderance to the approach of a ligated metal atom as does the ground state conformation of hexaethylbenzene.

Nevertheless, we were unable to synthesise and isolate an authentic chromium tricarbonyl complex of **1**. In contrast, simply refluxing **1** with an excess of molybdenum hexacarbonyl in *n*-heptane under nitrogen for five days gave tricarbony[η^6-1,3,5-triethyl-2,4,6-*tris*(trimethylsilylmethyl)benzene]molybdenum(0), (**2**), as yellow green crystals, reasonably stable as the solid in air, but oxidatively unstable in solution.

Photolysis of **2** with *cis*-cyclooctene in toluene solution gave the golden yellow complex, dicarbonyl(η^2-*cis*-cyclooctene)[η^6-1,3,5-triethyl-2,4,6-*tris*(trimethylsilylmethyl)benzene]molybdenum(0), (**3**), which crystallised from 40 – 60° petroleum ether in two different morphologies, neither of which contained solvent of crystallisation: **3a**, monoclinic, space group $P2_1/n$; and **3b** orthorhombic, space group $P2_12_12_1$. The crystal and molecular structures of **3a** and **3b** were determined at – 177°C and – 175°C respectively and that of **3b** additionally at room temperature (Tables 1 – 4 and Figs. 1 – 4). In both **3a** and **3b** all three ethyl groups project from the same face of the benzene ring and are proximal to the molybdenum atom, the benzene ring is planar, the individual C-C (arene) bond lengths are within the normal range, and there is no bond lengths alternation. The co-ordinated arene thus retains a conformation approximating to the ground state conformation calculated for the free molecule. However, there is evidence of very substantial steric strain in the co-ordinated arene of **3**: first, the C_{ar}-CH_2-CH_3 bond angles (Table 4) of the ethyl groups approach values more appropriate to those expected for sp^2 hybridised carbon atoms (**3a**, average value 117.6°; **3b**, average value 118.1°, with a maximum of 119.4° observed for the ethyl group closest to the coordinated *cis*-cyclooctene); second, the methylene carbons of the proximal ethyl groups are forced onto the distal side of the benzene ring plane. The retreat onto the distal face is particularly notable for C (7) and C (9) which are closest to the alkene carbons of the *cis*-cyclooctene moiety, and C (9) is at a distance of 0.26 Å from the least squares plane of the benzene ring carbons in **3b**. A similar, albeit much less marked, retreat of the methylene carbons of non-eclipsed ethyl groups to the other side of the benzene ring has been observed for tricarbonyl(η^6-hexaethylbenzene)-molybdenum(0) [14]. As with that complex, the carbonyls of **3** efficiently eclipse those benzene ring carbons which bear distal alkyl groups. The molybdenum atom is only slightly offset towards C (5); the resulting tilt angle, defined as the angle between the normal to the least squares plane of the benzene ring and the vector from the ring centroid to the molybdenum atom [14], is quite modest at 1.6° for **3a** and 1.8° for **3b**. It might have been anticipated that steric repulsion between the co-ordinated *cis*-cyclooctene and the proximal ethyl groups located on C (1) and C (3) would lead to a rather larger tilt angle, but clearly interactions between the carbonyls and their adjacent proximal ethyl groups prevent its full development.

The major difference between the molecular structures **3a** and **3b** concerns the inclination of the alkene double bond with respect to the benzene ring least squares plane. In **3a** the carbon-carbon bond is almost parallel to the benzene ring plane and the angle between bond C (27) and C (28) and the normal to the plane is 86.3°, whereas in **3b** it is significantly tilted, with the corresponding angle being 74.8°.

This inclination in **3b** may be due less to intramolecular effects than to intermolecular interactions although it persists unchanged at room temperature despite an increase of nearly 6% in the cell volume compared with that at − 175°. Nevertheless, whether of intra- or intermolecular origin, this inclination should reduce the overlap efficiency between the molybdenum orbitals and the unfilled π^*-antibonding orbital of the carbon-carbon double bond. This should have the effect of lengthening the Mo-C(27) and Mo-C(28) bond length while reducing that of C(27)-C(28), but within the standard deviations, these distances are the same for both **3a** and **3b**. Moreover, for both molecular structures there is only a very small increase in the bond length C(27)-C(28) (**3a**, 1.382(13); **3b**, 1.385(16) Å) compared with that calculated for free *cis*-cyclooctene (1.333 Å), suggesting that back donation makes a relatively unimportant contribution to the bonding between the molybdenum atom and the alkene ligand in these complexes. This conclusion is further supported by NMR results; the $^{1}J\,^{13}$C-^{1}H coupling constant of the alkene protons of complex 3 ($J = 154.4$ Hz) is almost identical to that of the free ligand ($J = 154.1$ Hz).

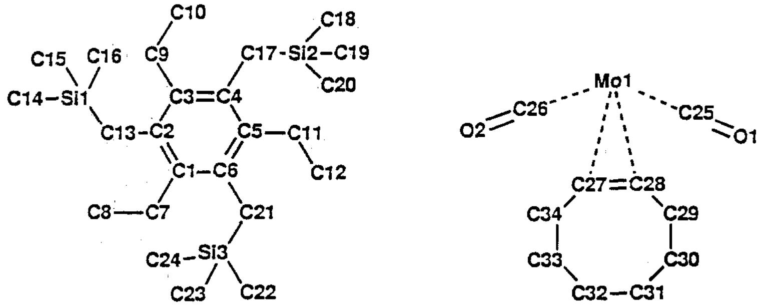
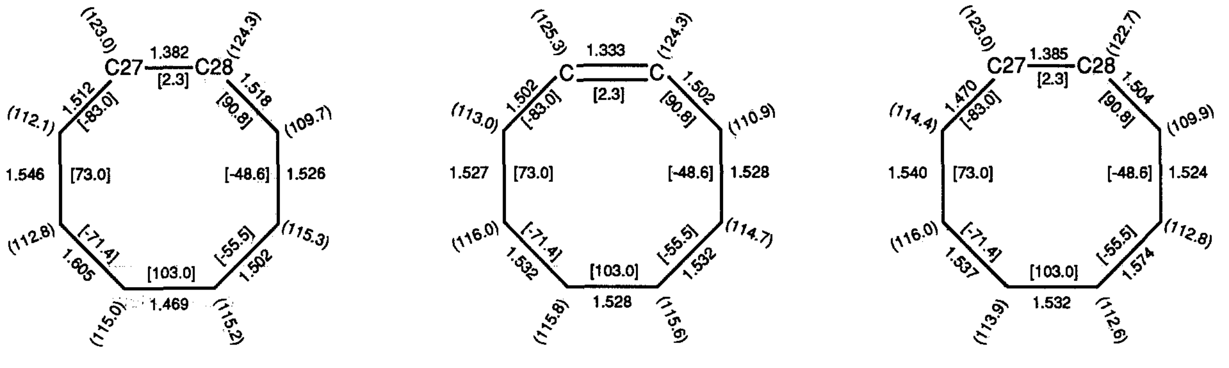


Fig. 3. Atom numbering of the X-ray structures **3a** and **3b**



3a **3b**

Fig. 4. Bond distances, bond angles (in parenthesis), and torsional angles (in brackets) calculated for *cis*-cyclooctene [2], and found for **3a** and **3b**

Table 1. Fractional atomic co-ordinates [$\times 10^4$] and isotropic temperature co-efficients[a]; [$\text{Å}^2 \times 10^4$] for the non hydrogen atoms in the crystal structure of **3 a** estimated standard deviations in parentheses

	x/a	y/b	z/c	U_{eq}
MO1	1 140 (1)	6 466 (1)	1 310 (0)	114 (5)
SI1	−1 912 (3)	8 601 (2)	2 112 (1)	246 (19)
SI2	−2 949 (3)	6 548 (2)	− 422 (1)	198 (18)
SI3	2 369 (3)	8 544 (2)	− 271 (1)	233 (18)
C1	921 (10)	7 749 (5)	1 208 (5)	102 (27)
C2	− 288 (10)	7 495 (6)	1 495 (5)	145 (29)
C3	−1 141 (10)	6 972 (6)	1 162 (5)	141 (28)
C4	− 752 (10)	6 698 (5)	556 (5)	133 (29)
C5	528 (10)	6 916 (5)	267 (5)	69 (25)
C6	1 310 (10)	7 432 (5)	598 (5)	123 (27)
C7	1 718 (9)	8 375 (5)	1 470 (5)	129 (28)
C8	3 002 (11)	8 211 (6)	1 896 (5)	219 (32)
C9	−2 526 (10)	6 773 (5)	1 440 (5)	111 (28)
C10	−2 611 (12)	6 083 (6)	1 834 (6)	247 (32)
C11	939 (10)	6 635 (5)	− 391 (5)	154 (28)
C12	1 912 (11)	6 012 (6)	− 407 (6)	205 (30)
C13	− 734 (11)	7 789 (6)	2 139 (5)	205 (31)
C14	−1 018 (14)	9 420 (8)	2 408 (7)	571 (46)
C15	−2 585 (12)	8 771 (7)	1 265 (6)	417 (39)
C16	−3 362 (10)	8 404 (6)	2 663 (5)	307 (33)
C17	−1 676 (10)	6 181 (5)	207 (5)	121 (28)
C18	−3 806 (12)	7 369 (6)	− 125 (6)	306 (34)
C19	−2 228 (11)	6 785 (6)	−1 215 (5)	268 (33)
C20	−4 223 (12)	5 814 (6)	− 548 (6)	306 (34)
C21	2 617 (10)	7 724 (5)	269 (5)	136 (29)
C22	629 (11)	8 949 (7)	− 167 (6)	356 (36)
C23	2 578 (11)	8 300 (6)	−1 144 (5)	295 (34)
C24	3 722 (11)	9 196 (6)	− 22 (6)	322 (35)
C25	921 (11)	5 481 (6)	1 163 (5)	200 (29)
O1	719 (7)	4 863 (4)	1 055 (4)	312 (21)
C26	3 014 (10)	6 277 (5)	1 150 (5)	134 (28)
O2	4 203 (7)	6 176 (4)	1 020 (3)	279 (21)
C27	2 035 (9)	6 492 (7)	2 385 (4)	200 (25)
C28	803 (10)	6 116 (5)	2 375 (5)	102 (26)
C29	662 (11)	5 329 (5)	2 560 (5)	203 (29)
C30	415 (11)	5 265 (6)	3 290 (5)	266 (31)
C31	1 436 (12)	5 656 (7)	3 720 (7)	489 (39)
C32	2 891 (12)	5 476 (7)	3 613 (6)	421 (37)
C33	3 764 (11)	6 087 (6)	3 252 (5)	362 (35)
C34	3 418 (9)	6 137 (6)	2 515 (5)	176 (29)

[a] The isotropic temperature factor has the form $T = \exp[-8\pi^2 U_{iso}(\sin^2\Theta/\lambda^2)]$. The equivalent isotropic temperature coefficient was calculated as one third of the trace of the orthogonalised U_{ij}-matrix

Table 2. Fractional atomic co-ordinates [$\times 10^4$] and isotropic temperature co-efficients[a] [$Å^2 \times 10^4$] for the non hydrogen atoms in the crystal structure of **3 b**; estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*	U_{eq}
MO1	8 651 (1)	273 (1)	1 292 (1)	107 (5)
SI1	4 037 (3)	443 (3)	1 013 (2)	217 (22)
SI2	7 230 (3)	654 (3)	3 301 (2)	170 (20)
SI3	7 540 (3)	4 014 (3)	1 516 (2)	176 (20)
C1	7 038 (11)	1 411 (9)	1 102 (5)	88 (28)
C2	6 555 (10)	507 (8)	1 298 (6)	162 (28)
C3	6 864 (10)	176 (10)	1 829 (5)	115 (27)
C4	7 750 (11)	629 (9)	2 124 (5)	158 (30)
C5	8 287 (11)	1 553 (9)	1 930 (5)	104 (28)
C6	7 908 (11)	1 903 (9)	1 431 (5)	147 (31)
C7	6 593 (11)	1 886 (9)	593 (5)	139 (31)
C8	7 197 (12)	1 618 (11)	61 (5)	222 (34)
C9	6 166 (11)	− 704 (8)	2 089 (5)	119 (28)
C10	6 598 (11)	−1 740 (9)	2 014 (5)	154 (31)
C11	9 127 (11)	2 126 (10)	2 287 (5)	191 (32)
C12	10 448 (12)	1 937 (10)	2 200 (5)	199 (32)
C13	5 636 (11)	− 22 (9)	973 (5)	177 (33)
C14	3 546 (15)	784 (11)	324 (5)	315 (37)
C15	3 930 (13)	1 552 (10)	1 479 (5)	329 (41)
C16	3 096 (12)	− 596 (9)	1 285 (6)	276 (33)
C17	8 103 (11)	202 (11)	2 683 (4)	146 (28)
C18	5 907 (11)	1 344 (10)	3 107 (5)	168 (31)
C19	8 166 (12)	1 458 (11)	3 734 (7)	332 (36)
C20	6 835 (12)	− 513 (10)	3 695 (7)	330 (36)
C21	8 392 (11)	2 890 (8)	1 242 (6)	200 (31)
C22	6 564 (13)	3 648 (11)	2 086 (6)	273 (37)
C23	8 646 (15)	4 906 (11)	1 744 (6)	379 (39)
C24	6 595 (11)	4 585 (10)	980 (5)	204 (33)
C25	9 816 (11)	− 446 (10)	1 699 (5)	173 (31)
C26	9 943 (14)	901 (12)	930 (6)	337 (40)
O1	10 497 (8)	− 902 (7)	1 961 (3)	197 (22)
O2	10 737 (9)	1 328 (8)	729 (4)	308 (26)
C27	8 764 (12)	− 609 (9)	457 (5)	184 (30)
C28	8 311 (11)	−1 222 (9)	860 (5)	119 (30)
C29	8 919 (11)	−2 166 (9)	1 042 (5)	152 (31)
C30	8 459 (14)	−3 053 (10)	715 (5)	264 (36)
C31	8 449 (13)	−2 849 (11)	85 (5)	277 (37)
C32	9 688 (13)	−2 624 (11)	− 141 (6)	271 (37)
C33	9 885 (13)	−1 518 (10)	− 286 (6)	267 (36)
C34	9 921 (11)	− 784 (10)	197 (5)	188 (32)

[a] The isotropic temperature factor has the form $T = \exp[-8\pi^2 U_{iso}(\sin^2\Theta/\lambda^2)]$. The equivalent isotropic temperature coefficient was calculated as one third of the trace of the orthogonalised U_{ij}-matrix

Table 3. Selected bond distances (Å) and bond angles (°) for **3a** and **3b**[a, b]

	3a	**3b**
Mo-C1	2.403 (9)	2.416 (12)
Mo-C2	2.394 (19)	2.383 (11)
Mo-C3	2.415 (10)	2.412 (11)
Mo-C4	2.416 (10)	2.333 (12)
Mo-C5	2.364 (9)	2.358 (12)
Mo-C6	2.322 (10)	2.359 (12)
Mo-C25	1.867 (10)	1.909 (13)
Mo-C26	1.883 (9)	1.901 (16)
Mo-C27	2.357 (9)	2.371 (12)
Mo-C28	2.309 (10)	2.294 (12)
C25-O1	1.186 (13)	1.173 (14)
C26-O2	1.201 (12)	1.171 (17)
C1-C2	1.402 (14)	1.411 (15)
C2-C3	1.440 (14)	1.420 (16)
C3-C4	1.402 (14)	1.375 (16)
C4-C5	1.442 (14)	1.455 (16)
C5-C6	1.392 (13)	1.382 (16)
C6-C1	1.439 (14)	1.431 (16)
C25-Mo-C26	84.0 (4)	86.6 (6)
C2-C2-C3	120.2 (9)	119.1 (11)
C2-C3-C4	120.4 (9)	121.7 (11)
C3-C4-C5	120.6 (9)	120.2 (11)
C4-C5-C6	117.2 (9)	116.7 (11)
C5-C6-C1	123.9 (9)	123.9 (11)
C6-C1-C2	117.5 (9)	117.7 (11)
C1-C7-C8	117.4 (8)	118.2 (10)
C3-C9-C10	117.6 (8)	119.4 (10)
C5-C11-C12	117.7 (8)	116.7 (11)

[a] From data collected at −177°C for **3a** and −175°C for **3b**

[b] Standard deviations in parentheses

However, in the similar complex, dicarbonyl(η^6-hexaethylbenzene)(η^2-maleic anhydride)molybdenum(0), a back donation contribution seems to be much more important to the metal-ligand interaction as reflected in a considerably greater carbon-carbon double bond length (1.485 Å) than in non-coordinated maleic anhydride (1.337 Å) [12]. Of the other *cis*-cyclooctene complexes whose molecular structures have been reported, only for bis(η^2-*cis*-cyclooctene)(μ-dichloro)[bis(bis(trimethylsilylmethyl)phosphine]dirhodium(I) is there substantial lengthening of the alkene double bond (1.413 Å) [8]; the gold(I) complex, and the other rhodium(I) complex [7] having values of 1.38 Å and 1.37 Å respectively almost the same as those observed for **3a** and **3b**. The copper(I) complex value is virtually unchanged at 1.34 Å [10].

The conformation of the complexed *cis*-cyclooctene in both **3a** and **3b** is remarkably similar to that calculated to be the ground state conformation of the

Table 4. Selected distances (Å) from the mean plane of the arene ring carbon atoms for **3a** and **3b**

Atom	**3a**	**3b**
C1	0.025	0.008
C2	−0.020	−0.038
C3	0.003	0.047
C4	0.021	−0.026
C5	−0.016	−0.005
C6	−0.007	0.013
Mo	−1.917	−1.912
C7	0.242	0.161
C8	−0.994	−1.096
C9	0.121	0.261
C10	−1.152	−0.916
C11	0.037	0.112
C12	−1.255	−1.188
C27	−3.339	−3.541
C28	−3.251	−3.178

[a] From data collected at −177°C for **3a** and −175°C for **3b**

isolated free molecule [1, 2]. Such an unsymmetrical twist conformation is best described as being intermediate between chair and boat forms and indeed could be regarded as a point on the interconversion itinerary between both those idealised conformers [15]. Nevertheless, it is the only conformer that has so far been found for coordinated *cis*-cyclooctene. It occurs even for the dirhodium(I) complex [8] where the more substantial lengthening of the carbon-carbon bond might have been expected to exacerbate the severe congestion in the ring and perhaps lead to conformational change. Fig. 4 shows the bond lengths, angles, and torsional angles calculated for *cis*-cyclooctene [2] and of the coordinated moiety found for **3a** and **3b**. In the room temperature molecular structure for **3b**, the *cis*-cyclooctene conformation differs slightly from its low temperature structure, but only in the torsional angles of that side which is tilted closer to the arene.

It is difficult to explain the surprising stability of **3**; both the coordinated organic moieties are quite clearly sterically very strained, and there appears to be relatively little back donation to the *cis*-cyclooctene double bond to relieve the high electron density of the molybdenum atom.

Experimental Part

NMR spectra were recorded using a Bruker WH 360 spectrometer operating at 90.56 MHz for ^{13}C. All NMR samples were filtered under N_2 through a grade 3 glass sinter, freeze-thaw degassed, and sealed in 10 mm (outside diameter) tubes.

1,3,5-Triethyl-2,4,6-tris(trimethylsilylmethyl)benzene (**1**)

To a degassed solution of 3.2 g (10.4 mmol) of 1,3,5-*tris*(chloromethyl)-2,4,6-triethylbenzene and 4.02 g (37 mmol) of trimethylchlorosilane in 100 ml of dry *THF* at room temperature was added 1.44 g

(36.8 mmol) of potassium. The stirred mixture was heated under reflux for 6 h. Ethanol (5 ml) was carefully added to the cooled reaction mixture and the solvent then removed under reduced pressure. The residue was suspended in chloroform, transferred to a separating funnel and washed three times with water. The organic layer was dried over sodium sulphate and the solvent removed under reduced pressure. The residual solid was recrystallised from a mixture of *n*-hexane and 3% ethyl acetate to remove unreacted starting material. The solvent of the mother liquor was removed under reduced pressure and the residue chromatographed on silica (eluent, *n*-hexane/1% ethyl acetate) and gave 1.53 g (35%) yield of **1**, m.p. 70 – 71°C. ^{13}C-NMR (CD_2Cl_2): δ (ppm) 133.2 (arene), 132.5 (arene), 23.3 (CH_2), 17.9 (CH_2), 13.3 (CH_3), – 0.2 [$Si(CH_3)_3$]. MS *m/e* 420 (M^+, 21), 405 (3.5), 347 (3.3), 73 (100%).

Tricarbonyl(η^6-1,3,5-triethyl-2,4,6-[tris(trimethylsilylmethyl)benzene]molybdenum(0) (**2**)

Molybdenum hexacarbonyl (0.67 g, 2.54 mmol) was refluxed with **1** (0.71 g, 1.70 mmol) in *n*-heptane under nitrogen for five days. The solution initially turned yellow but a black precipitate eventually formed. After cooling the reaction mixture, the supernatant liquid was filtered off and the black residue extracted with two 50 ml portions of acetone, the extracts filtered under nitrogen and the filtrate evaporated to give yellow-green crystals of **2** (0.15 g, 15% yield). (Anal. calcd. for $C_{27}H_{48}MoSi_3O_3$: C 54.1, H 8.0; found C 54.3; H 8.1 %). ^{13}C-NMR (CD_2Cl_2): δ (ppm), 226.2 (carbonyls), 122.6 (arene), 111.9 (arene), 21.9 (CH_2), 21.4 (CH_2), 19.6 (CH_3), – 0.6 [– $Si(CH_3)_3$].

Dicarbonyl(η^2-cis-cyclooctene)[η^6-1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)-benzene]molybdenum(0) (**3**)

A freeze-thaw degassed benzene solution of **2** (0.5 g, 0.84 mmol) and *cis*-cyclooctene (10 ml) was photolysed by u.v. irradiation for 2 h. The orange yellow solution was filtered under nitrogen and the solvent and excess *cis*-cyclooctene evaporated under reduced pressure. The residue was extracted with 40 – 60° petroleum ether and purified twice by medium pressure chromatography (230 – 400 mesh silica gel (Merck 9385), eluent 60 – 80° petroleum ether/2% ethyl acetate) under nitrogen. Removal of the solvent gave yellow crystals of **3** (0.2 g 35% yield). An analytical sample was recrystallised from 40 – 60° petroleum ether by slow evaporation under nitrogen at 0°. (Anal. calcd. for $C_{34}H_{62}MoO_2Si_3$: C 59.9, H 9.1; found C 60.4, H 9.2 %). ^{13}C-NMR (CD_2Cl_2): δ (ppm), 238.2 (carbonyls), 119.0 (arene), 109.3 (arene), 60.6 (C = C), 33.5 (CH_2), 31.7 (CH_2), 26.7 (CH_2), 24.1 (CH_2), 20.4 (CH_2), 17.3 (CH_3), 0.4 [– $Si(CH_3)_3$].

X-Ray Data Collection, Solution, and Refinement of the Structures

X-Ray Analysis of **3 b**. Crystals were obtained from petroleum ether (40 – 60°C). A dark yellow crystal of size 0.2 × 0.3 × 0.3 mm was used for data collection. Cell parameters were determined by least squares refinement of the angular positions of 38 reflections in the range $9 \leqslant 2\Theta \leqslant 13°$: $a = 11.269(4)$, $b = 13.366(4)$, $c = 24.580(14)$ Å, $V = 3702$ Å^3, at 98(1) K, space group $P2_12_12_1$, $Z = 4$ for $C_{34}H_{62}MoSi_3O_2$, $d_{(calc)}(98\text{ K}) = 1.125$ g cm^{-3}.

Data were collected on a modified STOE four-circle-diffractometer equipped with a NONIUS low temperature device using MoK_α-radiation ($\lambda = 0.71069$ Å, graphite monochromator) at 98 (13) K [7 620 reflections, 6 412 unique, 4 639 with $I > 4\sigma(I)$] were measured with ω-scan technique ($\Delta\omega = 1.2°$) to a limit of $2\Theta = 50°$. Three standard reflections were periodically monitored (every 100 reflections). Their intensities fluctuated by less than 5.5%. Intensity data were corrected for Lorenz and polarisation effects. The structure was solved by locating the Mo- and Si-atoms from a Patterson map. A subsequent tangent expansion and two cycles of structure optimisation [16] yielded the positions of all non hydrogen atoms. The positions of hydrogen atoms were calculated on the basis of stereochemical plausibility. Full matrix leastsquares refinement [17] involved positional coordinates for all non-hydrogen atoms plus isotropic atomic displacement parameters (ADPs) for C, H and O and anisotropic

ADP's for Mo and Si. An empirical absorption correction [18] ($\mu_{\mathrm{MoK}\alpha} = 4.7\,\mathrm{cm}^{-1}$) was applied following isotropic refinement of all atoms. Refinement of anisotropic ADPs for all non-hydrogen atoms led to marginal improvement of the *R*-factor (by about 0.005). We choose to report the result of the refinement of isotropic ADPs for C and O because of the considerably better parameter to observations ratio (243 : 4 639 versus 423 : 4 639) and the fact that the refined ADPs for several C-atoms yielded non-positive definite libration ellipsoids. Both, the only marginal improvement of the *R*-factor and the non-positivity of libration ellipsoids are not uncommon for low temperature structures.

Refinement converged at $R = 0.059$, $R_W = 0.057$ for 243 parameters and 4 639 observations ($w_i = 1/\sigma^2(F_i) + aF_i^2$, $a = 0.000016$). Standard deviations for bond lengths range between 0.012 Å (C-Mo bonds) and 0.016 Å (C-C bonds). Highest peak in a final difference density Fourier synthesis 1.3 eÅ^{-3}. Atomic coordinates and isotropic (or equivalent-isotropic) ADPs are given in Table 1.

A room temperature (293 K) data set was collected using a STOE Stadi II diffractometer (3 638 reflections collected yielded 1 248 observed unique data, corrected for absorption). Standard intensities decreased by 10% during data collection as the crystal blackened and decomposed. No allowance was made for this decomposition during data processing. Cell parameters: $a = 11.404(12)$, $b = 13.666(16)$, $c = 25.123(14)$ Å, $V = 3\,915$ Å^3, space group $P2_12_12_1$, $Z = 4$, $d_{\mathrm{calc}}(293\,\mathrm{K}) = 1.120\,\mathrm{g\,cm}^{-3}$.

Using the coordinates from the low-temperature structure as a starting model, an acceptable refinement [17] was obtained using anisotropic ADPs for Mo, Si, and the carbonyl groups. No hydrogen atoms were included. Residual $R = 0.085$. No disorder was detected at 293 K, nor was there any major difference from the structure obtained at 98 K.

X-Ray Analysis of **3 a**. Crystals of **3 a** were obtained from petroleum ether (40 – 60°C). **3 a** crystallises in the centrosymmetric space group $P2_1/n$, $Z = 4$ for $C_{34}H_{62}MoSi_3O_2$; crystal size 0.5 × 0.5 × 0.15 mm; cell parameters were determined by least squares refinement of the angular positions of 25 reflections in the range of $9 \leqslant 2\Theta \leqslant 18°$: $a = 9.684(4)$, $b = 18.589(8)$, $c = 20.520(15)$ Å, $\beta = 90.98(4)°$ at 96(1) K, $V = 3\,693$ Å^3, $d_{\mathrm{calc}}(96\,\mathrm{K}) = 1.228\,\mathrm{g\,cm}^{-3}$.

Data collection, structure solution and refinement as above; 4 132 reflections [3 654 unique, 1 938 with $I < 4\sigma(I)$] collected with ω-scan technique ($\Delta\omega = 1.0°$) to a limit of $2\Theta = 40°$; intensity fluctuations of the standard reflections less than 5%. $R = 0.039$; $R_w = 0.036$ (weighting system as above with $a = 0.0$, 1 938 observations, 243 parameters). Highest peak in last ΔF-Fourier-synthesis 0.43 eÅ^{-3}. Standard deviations of bond lengths range betwen 0.01 (C-Mo) and 0.016 Å (C-C). Atomic coordinates and isotropic ADPs are given in Table 2.

Supplementary Material Available. Positional and atomic displacement parameters for all atoms (including H-atoms at calculated positions) in the low temperature crystal structure of **3 a** and **3 b**, (Tables 5 and 6) as well as structure factors are available on request from the authors. Ordering information is given on any masthead page.

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