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[20] **1a** and **1b** were treated with $[Rh(acac)(CO)_2]$ in CD_3OD, giving rhodium complexes with the phosphacalix[4]arenes acting as ligands. Complexation was indicated by the ^{31}P NMR spectrum, for example, the **1b**/$[Rh(acac)(CO)_2]$ complex showed two doublets at $\delta = 45.2$ (J(P,Rh) = 173 Hz) and 45.7 (J(P,Rh) = 174 Hz).

[21] DMCD may form inclusion complexes with TPPTS, which are capable of transferring into the organic phase. An analogous formation of inclusion complexes between unmodified β- and γ-CDs and TPPTS has been proved: E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *New J. Chem.* **1999**, *23*, 469–472. Consequently, it is possible to leach out rhodium from the aqueous phase.

$[Mo(CH_3)_6]$ and $[Mo(CH_3)_7]^-$**

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More than two decades ago Wilkinson prepared $[W(CH_3)_6]$ and $[Re(CH_3)_6]$, which at the time were the only neutral hexamethyl transition neutral compounds.[1, 2] Later these compounds gained importance because they are classical examples for d^0 and d^1 complexes containing only σ-binding ligands, and therefore they should be not be octahedral, as predicted by several corresponding theoretical papers.[3–7] In the meantime the structures of $[Zr(CH_3)_6]^{2-}$,[8] $[W(CH_3)_6]$,[9] $[Re(CH_3)_6]$,[9] $[Nb(CH_3)_6]^-$,[10] $[Ta(CH_3)_6]^-$,[10] $[Ta(C_6H_5)_6]^-$,[11] and $[Ta(4\text{-}CH_3C_6H_4)_6]^-$[11] have been determined experimentally, and agree fully with the theoretical predictions: The structures are based on a trigonal prism, either regular as in $[Re(CH_3)_6]$, $[Ta(CH_3)_6]^-$, and $[Zr(CH_3)_6]^{2-}$, or more or less distorted trigonal prismatic as in $[W(CH_3)_6]$ and $[Nb(CH_3)_6]^-$ with retention of the C_{3v} symmetry.

The structure of $[W(CH_3)_6]$ has been of special interest because it is strongly C_{3v}-distorted trigonal prismatic, having nonequivalent W–C bonds; that is, three longer ones which have a very narrow angle to each other, and three shorter ones with a larger angle to each other. According to the latest theoretical calculation,[4] that has also predicted the experimental structure in detail, the C_{3v} distortions should be especially large in the case of $[Mo(CH_3)_6]$, $[Re(CH_3)_6]^+$, and $[Tc(CH_3)_6]^+$. All three molecules or cations, respectively, are presently unknown.

We report here on the preparation of $[Mo(CH_3)_6]$ from MoF_6 and $Zn(CH_3)_2$, as well as on its structure. This reaction pathway is so far the only one with reasonable yields. Oxidic ($MoOCl_4$) or starting materials with nonhexavalent Mo centers ($MoCl_5$) should be avoided. Common methylating agents other than $Zn(CH_3)_2$, such as $LiCH_3$, reduce MoF_6. $[Mo(CH_3)_6]$, prepared in this way, is an orange-brown crystalline compound at low temperatures, which is volatile in high vacuum, and thermally stable up to about 10 °C. It is very sensitive towards oxygen. Proof of its existence and structure stems mainly from a single-crystal X-ray structure determination (Figure 1). Single crystals were obtained by recrystallization from acetone at −80 °C. The crystal structure is notable for the existence of three crystallographically different, but otherwise essentially similar $[Mo(CH_3)_6]$ molecules. As in $[W(CH_3)_6]$ and $[Re(CH_3)_6]$, the intermolecular interactions can be considered as weak; the shortest Mo–Mo distances are 580 pm.[9] We concluded from the fact that the three crystallographically different molecules have essentially the same molecular structure that the latter is not influenced by packing effects but rather represents the structure of the free molecule (Table 1). Crystallographically it may be of interest that molecules I and III can be interconverted by a pseudo-inversion center, not however, molecule II with itself. This led to the choice of a noncentrosymmetric space group. Of the 54 different hydrogen atom positions all except one were located in difference Fourier maps and refined. None of

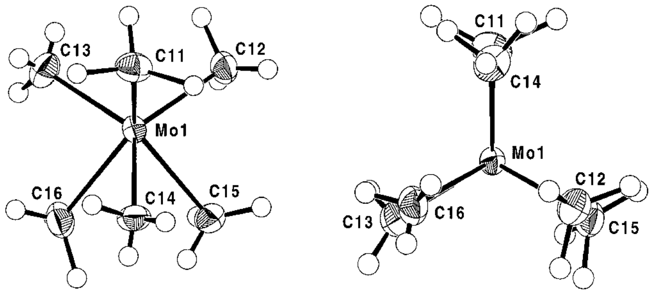

Figure 1. ORTEP representation of $[Mo(CH_3)_6]$, molecule I, 50 % probability ellipsoids, view perpendicular and along the threefold molecular axis. Because of the smaller angle to the molecular axis of the longer bonded methyl groups these appear closer to the molybdenum atom in the projection on the right-hand side. Distances [pm] and angles [°] (the corresponding values of $[Mo(CH_3)_6]$ II and $[Mo(CH_3)_6]$ III are given in parentheses): Mo1-C11 212.6(8) (208.8(6), 213.8(8)), Mo1-C12 210.3(7) (209.6(7), 211.3(5)), Mo1-C13 210.7(6) (211.8(6), 209.5(5)), Mo1-C14 220.0(7) (220.0(6), 216.7(8)), Mo1-C15 217.5(9) (218.8(6), 220.7(5)), Mo1-C16 219.5(6) (220.5(7), 219.7(6)); C11-Mo1-C12 93.6(3) (97.0(3), 96.1(3)), C11-Mo1-C13 93.8(4) (98.9(3), 96.6(3)), C12-Mo1-C13 97.5(3) (96.0(3), 98.2(2)), C14-Mo1-C15 75.2(3) (75.8(2), 75.7(2)), C14-Mo1-C16 76.9(3) (74.7(3), 74.7(3)), C15-Mo1-C16 75.1(3) (75.7(3), 74.2(2)).

Table 1. Structure of $[Mo(CH_3)_6]$ in the crystal, mean (angles are given only between C_{3v}-symmetry equivalent bonds) and calculated values.[4]

	$[Mo(CH_3)_6]$-I	$[Mo(CH_3)_6]$-II	$[Mo(CH_3)_6]$-III	calcd
Mo–C [pm]	211.2	210.1	211.5	213.6
	219.0	219.7	219.0	220.6
C-Mo-C [°]	94.9	97.3	96.9	97.3
	75.7	75.4	74.5	74.7

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these hydrogen positions gave any indications of agostic interactions.

The C_{3v} distortion of the approximate trigonal-prismatic molecules is clearly visible in Figure 1, and the mean distances and angles agree well with those from the theoretical predictions (Table 1). Also as predicted, bond length differences and angles between differently bonded methyl groups are somewhat larger than in $[W(CH_3)_6]$. This difference between the structures of $[Mo(CH_3)_6]$ and $[W(CH_3)_6]$ can be attributed to the relativistic effect, which in the case of $[W(CH_3)_6]$ is particularly strongly pronounced.[4]

The Raman spectrum of $[Mo(CH_3)_6]$ shows four well-separated CH valence vibrations. Under the assumption of local C_{3v} symmetry for each methyl group, two different kinds of methyl groups are indicated, if coupling between methyl groups is neglected. In the ^1H and ^{13}C NMR spectra only one line is found, which indicates nonrigidity of the molecule, resulting in equilibration of the methyl groups. According to calculations a regular trigonal-prismatic structure with six equivalent methyl groups is 39 kJ mol^{-1} higher in energy.

The seven-coordinate anion $[Mo(CH_3)_7]^-$ was prepared by treatment of $[Mo(CH_3)_6]$ with excess $LiCH_3$. $[Li(Et_2O)]^+[Mo(CH_3)_7]^-$ is isostructural with $[Li(Et_2O)]^+[W(CH_3)_7]^-$,[12] and the anion has accordingly a capped octahedral structure (Figure 2). This geometry is thought to have the smallest interligand repulsion energy for coordination number 7, and should prevail if this principle is structurally determining. However, in the case of main group compounds the pentagonal bipyramid is always found.

Whereas ab initio and density functional theory (DFT) calculations predict the experimentally determined structures very well, a simple explanation for the apparently abnormal structures of $[Mo(CH_3)_6]$ and $[W(CH_3)_6]$ is lacking, especially for d^0 complexes with exclusively σ-binding ligands in the case of coordination number 6. By applying Pauling's valence bond theory Landis et al. have found that under the assumption of pure sd^n hybridization bond angles of 180° should not exist between the resulting hybrid orbitals. Especially in the case of sd^5, angles between the hybrid orbitals of 63 and 117° are favored.[7] Thus, four structures can be constructed. One of these has C_{3v} symmetry and is quite similar to the $[Mo(CH_3)_6]$ structure, except the larger methyl groups increase the angle of 63° to about 75° for steric reasons. Thus the octahedron on which so much complex chemistry is based is here the most unlikely structure principle. The avoidance of interligand angles of 180° seems to be a general principle. In the case of the coordination number 5 ($[Mo(CH_3)_5]$,[13] $[Ta(CH_3)_5]$[12b,c, 13]), the square pyramid is favored; it has likewise no 180° arrangement of ligands in contrast to the trigonal bipyramid $[Sb(CH_3)_5]$.[12b,c] Also the capped octahedron with the coordination number 7 has no such arrangement of ligands, in contrast to the pentagonal bipyramid. Even if in some cases, as in $[Mo(CH_3)_7]^-$, the structure is the one with the smallest interligand repulsion, the latter model seems to play a secondary role with the compounds discussed here.

Experimental Section

All experiments were carried out under argon or in vacuum. Diethyl ether and *n*-pentane were dried with Na, acetone with K_2CO_3, and were degassed in vacuum. $Zn(CH_3)_2$ (1 M in *n*-heptane) purchased from Aldrich was separated from *n*-heptane by vacuum distillation.

$[Mo(CH_3)_6]$: MoF_6 (1.88 g, 8.96 mmol) was dissolved in Et_2O (30 mL). The bordeaux red solution was cooled to −130°C, and $Zn(CH_3)_2$ (1.34 g, 14.04 mmol) was added. The solution turned yellow, and colorless ZnF_2 precipitated. The mixture was warmed to −78°C and stirred for 12 h. Et_2O was pumped from the orange-colored solution, and the solid residue was extracted with a little acetone/*n*-pentane. The mixture was warmed to room temperature and sublimed into a liquid-nitrogen-cooled 8 mL glass ampule. Solvents were almost completely removed under vacuum, and the solid was dissolved in acetone. Orange-brown needles crystallized upon cooling from −55°C to −80°C from the dark red solution. These needles were stable up to 10°C, above which temperature the solid turned green; at room temperature sudden decomposition occurred under gas evolution and blackening. The yield was approximately 40%, losses were attributed to the sublimation procedure. Raman spectrum (solid, −70°C): $\tilde{\nu}$ = 3034 (1), 2996 (10), 2942 (12), 2856 (3), 1401 (8), 1205 (10), 1152 (20), 1129 (25), 999 (1), 810 (10), 737 (5), 667 (3), 631 (2), 583 (4), 521 (100), 496 (80), 439 (6), 413 (50), 353 (12), 301 (12), 258 (75), 232 (70), 140 (100) cm^{-1}; ^1H NMR ([D$_6$]acetone, −40°C): $\delta = 1.99$; ^{13}C NMR ([D$_6$]acetone): $\delta = 68.07$ (broad), $^1J_{C,H} = 126.9$ Hz. Crystal structure analysis: A crystal (0.4 × 0.4 × 0.2 mm) was mounted under nitrogen with cooling on a Bruker SMART CCD 1000 M diffractometer; Mo$_{K\alpha}$ irradiation, graphite monochromator, scan width ω of 0–3, 10 s per frame exposure time. A full sphere up to $2\theta = 66°$ was measured with 1800 frames. Data were reduced to the intensities, an empirical absorption correction was achieved by approximation of symmetry-equivalent reflections (Sad abs). Solution and refinement of the structure were performed with the Shelx programs.[14, 15] $a = 3123.67(8)$, $b = 628.75(1)$, $c = 1302.97(3)$ pm, $\beta = 92.623(2)°$, $V = 2.55636(10)$ nm^3, $Z = 12$, space group Cc, 14294 measured, 5450 independent reflections, 352 parameters, $R' = 0.0311$, $Rw^2 = 0.0814$.

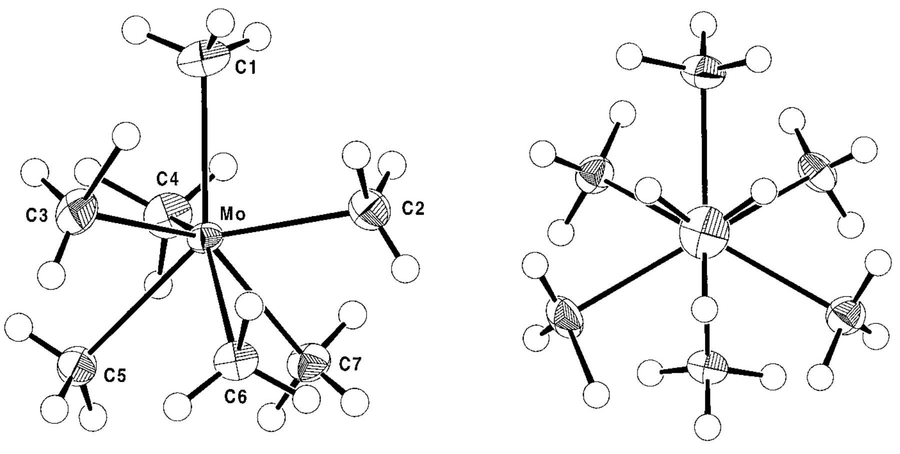

Figure 2. ORTEP representation of the $[Mo(CH_3)_7]^-$ ion in $[Li(Et_2O)]^+[Mo(CH_3)_7]^-$, 50% probability ellipsoids, view perpendicular and along the threefold molecular axis. Distances [pm] and angles [°]: Mo-C1 220.8(3), Mo-C2 216.9(3), Mo-C3 216.8(2), Mo-C4 217.1(3), Mo-C5 229.9(3), Mo-C6 230.1(3), Mo-C7 229.9(2); C1-Mo-C2 81.48(13), C1-Mo-C3 81.70(14), C1-Mo-C4 81.68(14), C1-Mo-C5 132.68(13), C1-Mo-C6 132.28(13), C1-Mo-C7 131.83(13).

$[LiO(C_2H_5)_2]^+[Mo(CH_3)_7]^-$: MoF_6 (1.09 g, 5.19 mmol) was dissolved in Et_2O (30 mL). The bordeaux red solution was cooled to −130°C and $Zn(CH_3)_2$ (1.04 g, 10.89 mmol) was added. The solution turned yellow, and colorless ZnF_2 precipitated. After the mixture had been stirred for 12 h at −78°C, ZnF_2 was filtered off. $LiCH_3$ (10 mL, 16 mmol; 1.6 M solution in Et_2O) was slowly added, the color of the solution turned light red. The reaction mixture was warmed to −15 °C and stirred for 1.5 h. At this temperature the Et_2O was pumped off and the residue was dissolved in a little *n*-pentane. With the help of a Teflon tube the solution was transferred into a 8-mL glass ampule. Upon cooling from −20 °C to −35 °C rubin red plates crystallized. Yield approximately 30 %, losses were attributed to the filtration procedure and to the recrystallization. ^1H NMR (*n*-pentane, −20 °C): $\delta = 1.91$; ^{13}C NMR: $\delta = 60.20$ (broad), $^1J_{C,H} = 123.4$ Hz. Crystal structure analysis: A crystal ($0.5 \times 0.4 \times 0.1$ mm^3) was mounted under nitrogen with cooling on the CCD diffractometer and measured as described above. Solution and refinement were performed with the Shelx programs.[14,15] $a = 694.6(3)$, $b = 1278.50(14)$, $c = 1733.6(4)$ pm, $V = 1.5395(7)$ nm^3, $Z = 4$, space group $Pbc2_1$, 17322 measured, 4603 independent reflections, 222 parameters, $R' = 0.0323$, $wR_2 = 0.0778$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135548 ($[Mo(CH_3)_6]$) and CCDC-135549 ($[LiO(C_2H_5)_2]^+[Mo(CH_3)_7]^-$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis of an Isolable Diphosphaisobenzene and a Stable Cyclic Allene with Six Ring Atoms**

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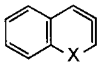
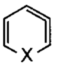
Dedicated to Professor Manfred Meisel
on the occasion of his 60th birthday

The synthesis of unusual, ring-strained isomers of benzene has been attracting increasing interest in the past few years. Besides cyclohexa-1,2,3-triene and cyclohexa-1-en-3-yne,[1] these species include cyclohexa-1,2,4-triene (**1**), an isobenzene that has been the subject of several theoretical studies.[2] In 1992, Christl et al. generated **1** for the first time using the Doering–Moore–Skattebøl method and confirmed its existence chemically by means of trapping reactions.[3] Compound **1** can also be formed by thermolysis of hexa-1,3-dien-5-yne.[4]

1



2a:X = CH_2
2b:X = CMe_2
2c:X = O



3a:X = S
3b:X = O

The benzo-condensed isobenzenes **2a**,[3] **2b**,[5] and the oxygen analogue **2c**[6] as well as the heteroatom-substituted isobenzene **3a**[7] have also been generated and trapped. Furthermore, substituted cyclohexa-1,2,4-trienes of the types **1** and **3b** have been discussed as nondetectable intermediates in the [4+2] cycloadditions of enynes and acylacetylenes, respectively, with alkynes.[8] We now report on the synthesis of the $1H$-$5\delta^2$-diphosphinine **8a**, which is stable at room temperature, and the cyclic allene **10** that can be prepared from it (see Scheme 2).

The starting material for the reactions described here is the previously unknown phosphatriafulvene **6** prepared from **4** and **5** (Scheme 1).[9] The structure of **6** was deduced from spectroscopic data as well as by comparison with the values reported for other known phosphatriafulvenes[9] and is not discussed in detail here. When **6** is allowed to react with the kinetically stabilized phosphaalkyne **7**[10] at 80 °C the isobenzene **8a** is obtained. This product is characterized by an

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