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# Pentamethylmolybdenum

**Beatrice Roessler, Sven Kleinhenz and Konrad Seppelt***

*Institut für Chemie der Freien Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany.*
*E-mail: seppelt@chemie.fu-berlin.de*

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**Pentamethylmolybdenum has been prepared and characterized by single crystal structure determination, EPR, and Raman spectroscopy.**

The total number of homoleptic[1] neutral metal methyl compounds is small. $Ti(CH_3)_4$ has never been obtained free of donor molecules.[2] $Nb(CH_3)_5$ and $Ta(CH_3)_5$ have been obtained in the pure state,[3] and the structure of the latter has been determined by electron diffraction.[4] $W(CH_3)_6$ and $Mo(CH_3)_6$ are known including their peculiar crystal structures,[5–7] as is $Re(CH_3)_6$.[6,8] Here we describe the formation of $Mo(CH_3)_5$.

In attempts to obtain $Mo(CH_3)_6$ by reacting $MoOCl_4$ with $Zn(CH_3)_2$[7] we have occasionally observed that in high vacuum a blue compound sublimed off into a −196 °C cold trap. We have been able to obtain a single crystal from this material which has been identified as $Mo(CH_3)_5$ by a single crystal structure determination. Subsequently we developed a preparative route from $MoCl_5$ (1.63 mmol) and a slight excess of $Zn(CH_3)_2$ (5.87 mmol) in 20 ml diethyl ether between −78 and −20 °C.[9] After pumping off all volatile materials at −78 °C, 15 ml *n*-pentane was added, and the suspension stirred for 30 min at −78 °C. At −20 °C the solvent was pumped off, and the tail of this vacuum distillation contained a light blue compound. Most of the solvent was pumped off at −78 °C and recrystallisation from $CF_3CH_2CF_3$ between −40 and −60 °C afforded turquoise needles, which turned black upon contact with traces of oxygen or upon warming above −10 °C. $Mo(CH_3)_5$ is thus thermally less stable than $Mo(CH_3)_6$.

The result of the single crystal structure determination is shown in Fig. 1† which shows that the molecule is a square pyramid. For comparison we also prepared $Ta(CH_3)_5$ and succeeded in obtaining single crystals of it by crystallizing a sample from $CF_3CH_2CF_3$ between −40 and −78 °C.† Both molecular structures are virtually identical, in spite of the fact that one is a $d^0$ and the other a $d^1$ system. The structural similarity is strikingly different from the $W(CH_3)_6$ ($Mo(CH_3)_6$)/$Re(CH_3)_6$ pair, where the $d^1$ system is different from the $d^0$ systems.[5,6]

The only, but still marginal, differences between the $Mo(CH_3)_5$ and $Ta(CH_3)_5$ structures are (i) the larger $C_{apical}$–M–$C_{basal}$ angles in $Mo(CH_3)_5$, and (ii) the larger bond length difference between apical and basal metal–C bonds for $Ta(CH_3)_5$.

We also calculated the structures of $Mo(CH_3)_5$ and $Ta(CH_3)_5$ using a density functional (DFT) approach, using electron core potentials[10] for Mo and Ta atoms and the 6-311 G(d,p) basis set for C and H.[11] The square pyramidal (*SPY*) structure is energetically strongly favored over the trigonal bipyramidal structure (*TBPY*). For the square pyramidal structures all geometric parameters have been refined independently. In order to obtain energetic and structural data for the trigonal bipyramidal structures one C–M–C angle has been fixed at 180°, while all other variables have been set free. The energy difference between the *SPY* and *TBPY* structures is calculated as 53.4 kJ $mol^{-1}$ for $Ta(CH_3)_5$, (*cf.* 32.2 kJ $mol^{-1}$ in an earlier calculation[12]). For $Mo(CH_3)_5$ the energy difference is even larger at 97.5 kJ $mol^{-1}$. At present it cannot be said with certainty if this large energy difference is a consequence of imperfect calculations, due to the open shell system. If it is real, this would indicate a strong steric activity of the $d^1$ electron which would be very unusual. Table 1 gives a summary of experimental and calculated structures of both compounds.

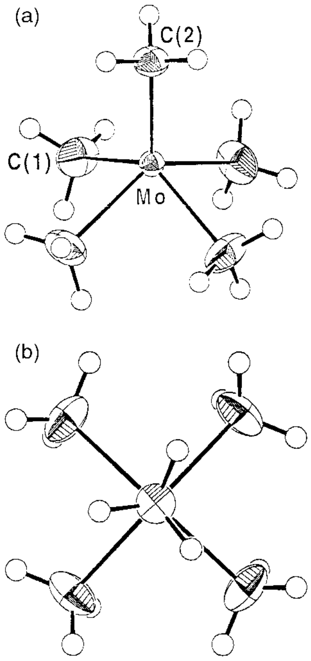

**Fig. 1** (a) Crystal structure of $Mo(CH_3)_5$. ORTEP with 50% probability ellipsoids. (b) View along the fourfold axis. The hydrogen positions of the apical methyl group are fourfold disordered and only one orientation is shown. The ORTEP for $Ta(CH_3)_5$ is essentially the same.

**Table 1** Bond lengths (pm) and angles (°) for the tetragonal pyramidal structures of $Mo(CH_3)_5$ and $Ta(CH_3)_5$

| | $Mo(CH_3)_5$ | | $Ta(CH_3)_5$ | | | |
|---|---|---|---|---|---|---|
| | X-Ray | DFT calculation[a] | X-Ray | Electron diffraction[b] | DFT calculation | MP2 calculation[c] |
| M–$C_{apical}$ | 206.8(1) | 209.9 | 207.3(14) | 211(2) | 214.7[a] | 215.4 |
| M–$C_{basal}$ | 211.1(1) | 215.2 | 215.0(7) | 218.0(5) | 218.2 | 218.7 |
| $C_{apical}$–M–$C_{basal}$ | 113.6(2) | 114.5 | 111.1(2) | 111.7(13) | 112.1 | 111.6 |
| $C_{basal}$–M–$C_{basal}$ | 80.8(1) | 80.0 | 82.6(2) | 82.9(9) | 81.8 | 82.2 |

[a] For details see text. [b] See ref. 4. [c] See ref. 14.

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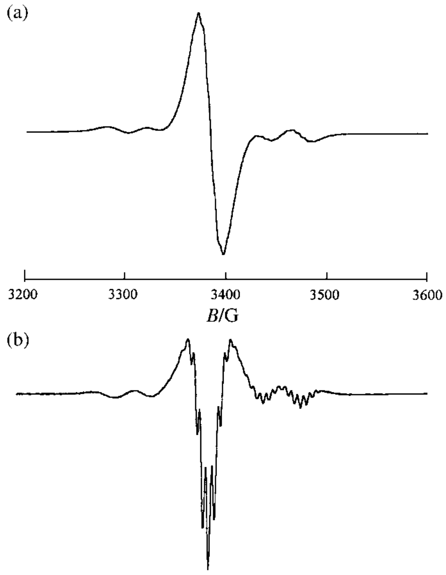

**Fig. 2** Isotropic EPR spectrum of $Mo(CH_3)_5$ in *n*-pentane solution at 130 K, 9.44 GHz. $g$ = 1,993, $a(^{95}Mo/^{97}Mo)$ = 4.8(1) mT, $a_H'$ = 0.54(1) mT: (a) first derivative and (b) second derivative spectrum.

The Raman spectrum of $Mo(CH_3)_5$ shows bands (relative intensities in parentheses) at 1181(10), 960(10), 90(50), 882(10), 783(10), 672(60), 620(30), 565(15), 523(100), 507(70), 451(15), 366(25), 308(100), 267(10) and 167(10) $cm^{-1}$ while the region above 2700 $cm^{-1}$ is obscured by the solvent pentane.

$Mo(CH_3)_5$ is paramagnetic and shows an EPR spectrum which is in full agreement with its structure (Fig. 2). Hyperfine splitting due to the two isotopes $^{95}Mo$ and $^{97}Mo$ (15.92 and 9.5% natural abundance), both with nuclear spin 5/2 and virtually identical gyromagnetic moments gives rise to six satellite resonances, two of which are obscured by the central line. The further fine structure is well resolved in the second derivative representation, and fits to a $^1H$ hyperfine structure due to an even number of equivalent hydrogen atoms and particularly well to a binomial distribution of 12th degree. Hyperfine structure due to the three apical hydrogen atoms is not resolved (Fig. 2). In agreement with this the calculation reveals that the unpaired electron has approximately two thirds Mo $4d_{z^2}$ and one third Mo $4d_{x^2-y^2}$ character.

## Notes and references

† *Crystal data*: $MoC_5H_{15}$: $M$ = 171.1, $a$ = 768.0(2), $c$ = 649.0(2) pm, $V$ = 382.8 × $10^6$ $pm^3$, tetragonal, space group $I4$, $Z$ = 2, $\mu$ = 1.6 $mm^{-1}$, 1306 measured, (including Friedel pairs), 340 independent reflections, 25 parameters, $R$ = 0.026, $wR^2$ = 0.047. Refinement in space group $I4/mm$ under the assumption of disorder of the C1 atoms gives essentially the same result. Refinement in space group $I4/mm$ without disorder and C1 in special position $x$,0,$z$ results in strongly elongated vibrational amplitudes for these atoms. Keeping the neighborhood of the basal methyl groups in adjacent molecules in mind the non-disordered but twinned solution has been chosen.

$TaC_5H_{15}$: $M$ = 256.1, $a$ = 784.8(1), $c$ = 647.3(1) pm, $V$ = 398.7 × $10^6$ $pm^3$, tetragonal, space group $I4$, $Z$ = 2, $\mu$ = 13.8 $mm^{-1}$, 883 measured, 802 independent reflections, 20 parameters, $R$ = 0.023, $wR^2$ = 0.059. In contrast to $Mo(CH_3)_5$ this structure clearly belongs to space group $I4$, the absolute structure has been determined, and there is no indication for twinning.

CCDC 182/1626. See http://www.rsc.org/suppdata/cc/b0/b000987n/ for crystallographic files in .cif format.

1 Homoleptic implies all ligands are the same.
2 $Ti(CH_3)_4$; S. Kleinhenz and K. Seppelt, *Chem. Eur. J*, 1999, **5**, 3573; K. H. Thiele, H. Windisch, H. Schumann and G. Kociok-Kühn, *Z. Anorg. Allg. Chem.*, 1994, **620**, 3829.
3 R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, 1974, **96**, 5288.
4 C. Pulham, A. Haaland, A. Hammel, K. Rypdal, H. P. Verne and H. V. Volden, *Angew. Chem.*, 1992, **104**, 1534; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1464.
5 A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 872.
6 S. Kleinhenz, V. Pfennig and K. Seppelt, *Chem. Eur. J.*, 1998, **4**, 1687; V. Pfennig and K. Seppelt, *Science*, 1996, **271**, 626.
7 B. Roessler and K. Seppelt, *Angew. Chem.*, 2000, **112**, 1326; *Angew. Chem., Int. Ed.*, 2000, **39**, 1259.
8 K. Mertis and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 1488.
9 The reaction of $MoCl_5$ with $LiCH_2Si(CH_3)_3$ affords $[(CH_3)_3SiCH_2]_3Mo{=}CH{-}Si(CH_3)_3$ and $((CH_3)_3SiCH_2)_3Mo{\equiv}C{-}Si(CH_3)_3$: R. A. Anderson, M. H. Chrisholm, J. F. Gibson, W. W. Reichert, I. P. Rothwell and G. Wilkinson, *Inorg. Chem.*, 1981, **20**, 3934.
10 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
11 Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. I. Martin, D. J. Fox, J. S. Binkley, J. D. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburg, PA, 1995.
12 T. A. Albright and H. Tang, *Angew. Chem.*, 1992, **104**, 1532; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1462.