

Preparation and Structures of Hexaphenyl- and Hexatolyltantalates(V)

Sven Kleinhenz, Mario Schubert, and Konrad Seppelt*

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin,
Fabeckstraße 34–36, D-14195 Berlin, Germany

Received November 14, 1996

Keywords: Hexaphenyltantalate / Hexatolyltantalate / Trigonal prismatic coordination / Transition metals / Structure elucidation

By reacting TaCl_5 with LiC_6H_5 and $\text{LiC}_6\text{H}_4\text{-4-CH}_3$ salts, the anions $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ and $\text{Ta}(\text{C}_6\text{H}_4\text{-4-CH}_3)_6^-$ were obtained in small yields. They were structurally characterized by low-

temperature single-crystal structure determination and found to have quite similar structures, which can be described as slightly distorted trigonal prismatic.

Hexacoordinated d^0 complexes containing ligands with no π -donor qualities are nonoctahedral. The most prominent example is $\text{W}(\text{CH}_3)_6$ which, according to its crystal structure, has a C_{3v} distorted trigonal prismatic orientation of the six methyl groups^[1]. Such a structure has been predicted or rationalized by a number of theoretical calculations^[2]. If one seeks a simple explanation one can argue that such a complex is highly electron deficient (only 12 valence electrons, and therefore far from the stable 18-electron count). Also the application of sd^5 hybridization within Pauling's bonding model leads, among others, to a C_{3v} distorted trigonal prism, whereas the alternative octahedral structure can be ruled out^[3]. The first experimental report on such a system was that on $[\text{Zr}(\text{CH}_3)_6]^{2-}$ by Morse and Girolami, where the zirconium environment is close to regular trigonal prismatic, though the structure may be influenced by interactions between the anion and the two $\text{Li}(\text{tmed})_2^+$ cations^[7]. It must also be borne in mind that the double negative charge, if only in part located on the methyl ligands, will cause an electrostatic repulsion effect that may be responsible for the less sterically crowded trigonal prismatic structure, as opposed to the C_{3v} distorted trigonal prismatic structure found in $\text{W}(\text{CH}_3)_6$.

The question is how the elements niobium and tantalum behave, lying between zirconium and tungsten in the periodic table. In spite of the enormous importance of tantalum organic compounds^[8], there is very little information about homoleptic organic compounds. $[\text{Ta}(\text{CH}_3)_5]$ and $[\text{Nb}(\text{CH}_3)_5]$ are known, and the structure of the former has been determined by electron diffraction to be square pyramidal^[9]. The same is true for $[\text{Ta}(\text{CH}_2\text{-C}_6\text{H}_5)_5]$, although a weak intramolecular contact by one phenyl group is observed^[10]. According to NMR measurements $[\text{Ta}(\text{CH}_3)_6^-]$ should exist^[11]. The situation is only a little better in the aromatic series: $[\text{Ta}(\text{C}_6\text{H}_5)_6^-]$ was first mentioned in a patent as a precursor for tantalum hydrides^[12], and it is also a precursor for $[\text{Ta}(\text{C}_8\text{H}_8)_3]^{13}$.

Reactions of NbBr_5 or TaBr_5 with LiC_6H_5 are described to be complex. By means of elemental analyses, UV spectra,

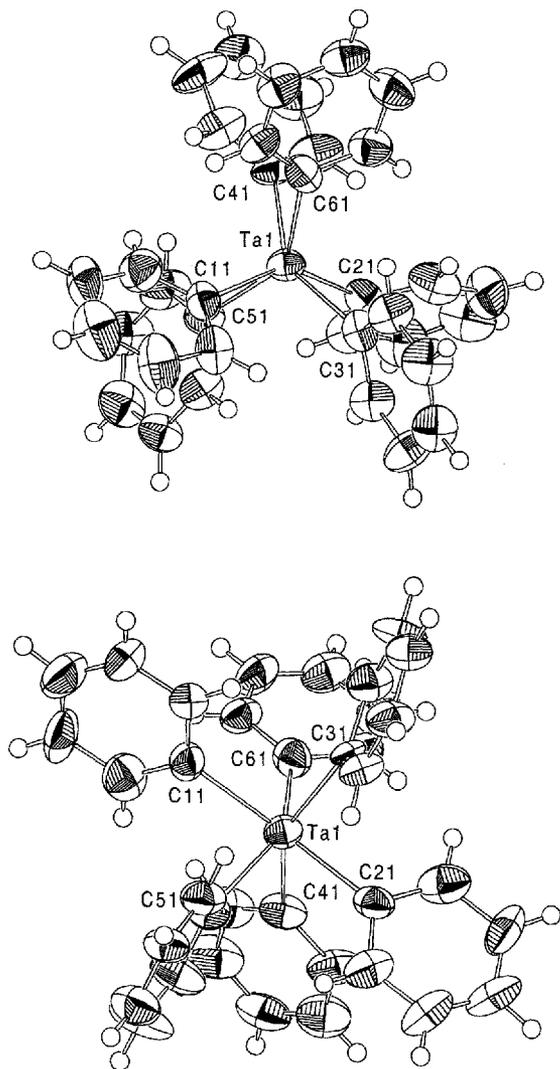
and magnetic measurements it was concluded that reduction to Nb^{II+} and Ta^{II+} is observed^[14]. Analytical evidence for $\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ was first achieved by B. Sarry and P. Velling in 1976^[15]. By use of NMR methods Sarry showed that $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ undergoes *ortho*-lithiation with excess LiC_6H_5 , resulting in benzyne complexes^[16]. This was proven later by a crystal structure study of $[\text{Ta}(\eta^2\text{-C}_6\text{H}_4)_2(\text{C}_6\text{H}_5)_4\text{Li}(\text{thf})_2]$. A benzyne complex is also observed in $[\text{Nb}(\eta^2\text{-C}_6\text{H}_4)_2(\text{C}_6\text{H}_5)_3] \cdot \text{LiC}_6\text{H}_5 \cdot \text{thf} \cdot \text{Li}(\text{thf})_4$ ^[17].

It was therefore clear from the outset of our investigation that TaAr_6^- materials should be quite unstable. We nevertheless aimed to synthesize these compounds, not only in order to establish the likely nonoctahedral coordination around tantalum(V), but also to investigate the influence of aromatic ligands as compared to simple methyl groups.

We started with the reaction between TaCl_5 and LiC_6H_5 . Yellow, brown, dark red, blue and violet colors occur, as has been described previously by Sarry et al. Only when we used benzene/diethylether as solvent and solid LiC_6H_5 at room temperature, did crystalline material of the composition $\text{Li}(\text{thf})_4^+ \text{Ta}(\text{C}_6\text{H}_5)_6^- \cdot 4 \text{C}_6\text{H}_6$ appear upon addition of THF to the solution. A salt containing the $\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ anion was obtained by reacting a TaCl_5 /pentane solution with a $\text{Li}(\text{4-C}_6\text{H}_4\text{-CH}_3)$ /ether solution. Upon cooling, yellow crystals of $\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+ \text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ were formed. Both crystalline materials slowly decompose under solvents, even at -78°C , and the yields of both crystalline materials are marginal. However, X-ray structure determination was possible at -153°C , and the results are shown in Figures 1 and 2 and Table 1. It is immediately obvious that these anions are closer to trigonal prismatic rather than octahedral. This is best seen if viewed along the approximate C_3 molecular axis, as shown in Figures 1b and 2b.

An ideal trigonal prismatic coordination can be described, besides the uniform bond length, by one bond angle alone. When one chooses the bond angle α between ligands within one hemisphere to be 85° , for example, the

Figure 1. Crystal structure of the $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ anion in $\text{Li}(\text{thf})_4^+ \text{Ta}(\text{C}_6\text{H}_5)_6^-$: Ortep plot, 50% probability ellipsoids; (a) view along the approximate threefold axis of the anion; (b) view perpendicular to the approximate threefold axis



angle β between close ligands of the other hemisphere comes out at 77.54° (see Figure 3). In $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ the corresponding angles are quite near to these values. A trigonal prismatic geometry can be changed into an octahedral one by rotating one triplet of ligands against the other triplet by 60° . The view along the C_3 molecular axis of $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ shows a rotation of the triplets of ligands by about 16° against each other. So the anion is closer to trigonal prismatic than to octahedral. The orientation of the phenyl ring planes is quite irregular and does not obey the highest possible S_6 symmetry (double propeller). This may account for the deviations in bond lengths and angles for the anion. For comparison: in octahedral $\text{Te}(\text{C}_6\text{H}_5)_6^-$ [18] and $\text{Bi}(\text{C}_6\text{H}_5)_6^-$ [19] the orientation of the phenyl ring planes is very regular: planes of adjacent phenyl groups are nearly perpendicular, and planes of opposite phenyl groups are nearly parallel. This array results in the almost perfect T_h symmetry of these main-group hexaphenyl complexes.

Figure 2. Crystal structure of the $\text{Ta}(4\text{-C}_6\text{H}_4\text{-CH}_3)_6^-$ anion in $\text{Li}_4\text{-Br}_3(\text{Et}_2\text{O})_7^+ \text{Ta}(4\text{-C}_6\text{H}_4\text{-CH}_3)_6^-$: Ortep plot, 50% probability ellipsoids; (a) view along the approximate threefold axis, of the anion; (b) view perpendicular to the approximate threefold axis

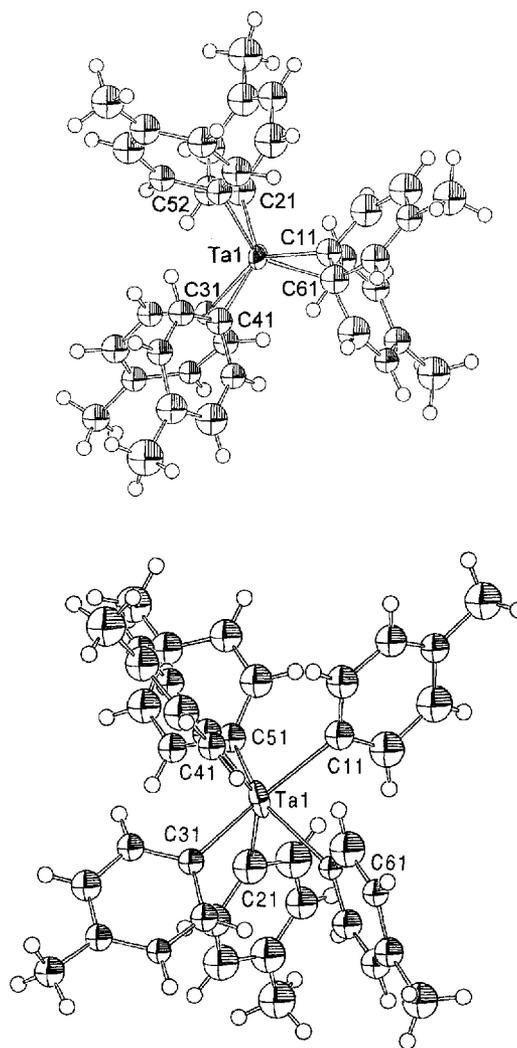
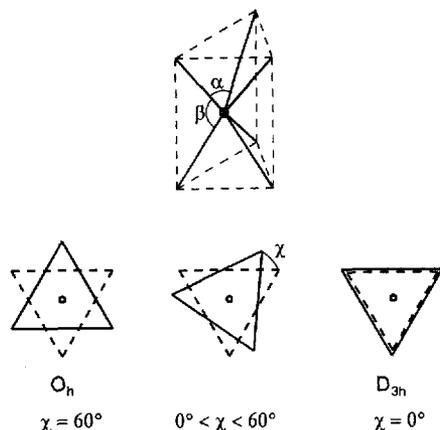


Table 1. Selected bond lengths (pm) and angles ($^\circ$) in the anions $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ and $\text{Ta}(4\text{-C}_6\text{H}_4\text{-CH}_3)_6^-$

	$\text{Ta}(\text{C}_6\text{H}_5)_6^-$	$\text{Ta}(4\text{-C}_6\text{H}_4\text{-CH}_3)_6^-$
Ta-C11	231(1)	226(2)
Ta-C21	227(1)	223(3)
Ta-C31	227(1)	227(2)
Ta-C41	226(1)	228(2)
Ta-C51	226(1)	219(2)
Ta-C61	227(1)	232(2)
C11-Ta-C21	146.1(4)	124(1)
C11-Ta-C31	85.0(4)	146(1)
C11-Ta-C41	124.0(5)	87(1)
C11-Ta-C51	76.1(4)	86(1)
C11-Ta-C61	85.8(4)	80(1)
C21-Ta-C31	78.1(4)	84(1)
C21-Ta-C41	83.2(4)	144(1)
C21-Ta-C51	87.4(4)	79(1)
C21-Ta-C61	122.7(5)	84(1)
C31-Ta-C41	146.5(4)	76(1)
C31-Ta-C51	120.1(4)	121(1)
C31-Ta-C61	89.6(4)	85(1)
C41-Ta-C51	86.1(4)	86(1)
C41-Ta-C61	77.5(4)	122(1)
C51-Ta-C61	142.9(4)	147(1)

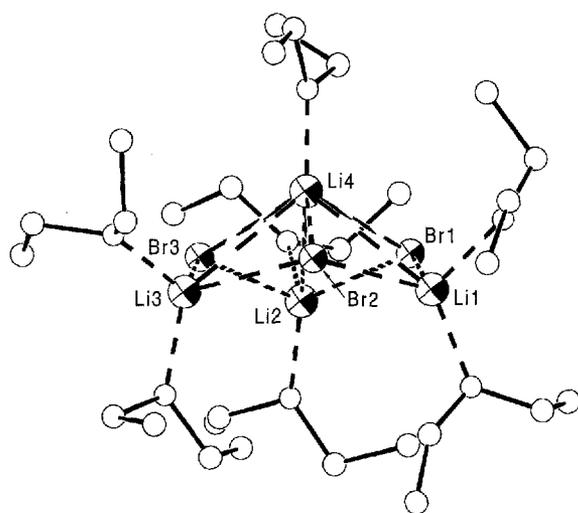
Figure 3. Definition of interligand angles, and interchange of a trigonal prism to an octahedron by changing one parameter



As shown in Figure 2b, the crystal structure of the $\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ anion is very similar, apart from the larger estimated standard deviations due to poor crystal quality. The rotation of the triplets of the tolyl ligands against each other along the C_3 molecular axis is also about 16° . In all, there is no noticeable difference between the $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ and $\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ anions with regard to their structure.

Although the formation of $\text{Li}(\text{thf})_4^+\text{Ta}(\text{C}_6\text{H}_5)_6^-$ is reproducible, we consider the crystallization of $\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$ to be accidental. This is already obvious from the type of the cations. The $\text{Li}^+(\text{thf})_4$ cation in $\text{Li}(\text{thf})_4^+\text{Ta}(\text{C}_6\text{H}_5)_6^- \cdot 4 \text{C}_6\text{H}_6$ has the usual tetrahedral coordination around Li^+ , as has been seen in many other cases. The cation $\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+$ is shown in Figure 3. The LiBr is clearly formed in the production of $\text{Li}(\text{4-C}_6\text{H}_4\text{-CH}_3)$. Both cations are similar in so far as they have essentially an organic surface. This together with their bulkiness and almost spherical shape guarantees that little interaction between cations and anions is observed, which in turn guarantees that the anionic shape is, if at all, only little perturbed by interionic interactions.

Figure 4. Crystal structure of the cation in $\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+\text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$: Ortep plot, 50% probability ellipsoids; non-marked atoms belong to ether molecules



This work was supported by the *Deutsche Forschungsgemeinschaft* and by the *Fonds der Chemischen Industrie*.

Experimental Section

All experiments were carried out under pure, dry argon. Solvents were dried over sodium, degassed and kept under argon. TaCl_5 was obtained by chlorination of Ta at $170\text{--}250^\circ\text{C}$ in a glass tube, and was purified by sublimation in a stream of elemental chlorine. TaCl_5 was obtained in 87% yield as a colorless powder, m.p. 215°C (lit. 216.2°C)^[20].

Solid $\text{C}_6\text{H}_5\text{Li}$ was obtained from a $\text{C}_6\text{H}_5\text{Li}$ solution in Et_2O ; this solution was prepared from Li wire and bromobenzene in Et_2O in the conventional manner. Pumping off the solvent resulted in a grey powder, which also contained LiBr . The LiC_6H_5 content was measured by titration and found to be 3.44 mmol/g .

p-Tolyl lithium in Et_2O solution was prepared from *p*-bromotoluene and lithium wire in the established manner.

Tetrakis(tetrahydrofurane)lithium Hexaphenyltantalate(V)-4 Benzene: A 250-ml glass vessel equipped with magnetic stirring bar and argon gas inlet was filled with 1.39 g (3.61 mmol) of TaCl_5 and 43.5 ml of abs. benzene. A yellow solution was obtained, which turned almost colorless upon addition of 1.5 ml of diethyl ether. The solution was cooled to 0°C , and 5.67 g of solid phenyllithium was added in the dark. From here on the reaction mixture was kept in the dark. The solution slowly turned black. The solid deposit that formed overnight at 0°C was filtered off, and 5.4 ml of tetrahydrofurane was added to the solution. This reaction mixture was held at 5°C for several days, and orange-yellow crystals formed at the bottom of the glass vessel. After longer standing these crystals disappeared. The yield could only be estimated to be below 10%.

With the help of a special device a suitable crystal was selected and mounted on an Enraf-Nonius CAD-4 four-cycle diffractometer at -153°C . Mo-K_α radiation, graphite monochromator. Lattice constants were obtained by fine adjustment of 25 selected reflections with $\theta > 20^\circ$. The Ψ -scan absorption correction was measured on 8 reflections with $\chi > 82^\circ$ in 10° steps of Ψ . Reflex

Table 2. X-ray structural analyses, details of solution and refinement of $\text{Li}^+(\text{thf})_4\text{Ta}(\text{C}_6\text{H}_5)_6^- \cdot 4 \text{C}_6\text{H}_6$ and $\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+, \text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$

	$\text{Li}^+(\text{thf})_4\text{Ta}(\text{C}_6\text{H}_5)_6^- \cdot 4\text{C}_6\text{H}_6$	$\text{Li}_4\text{Br}_3(\text{Et}_2\text{O})_7^+, \text{Ta}(\text{4-C}_6\text{H}_4\text{-CH}_3)_6^-$
formula	$\text{C}_{76}\text{H}_{86}\text{LiO}_4\text{Ta}$	$\text{C}_{70}\text{H}_{112}\text{Br}_3\text{Li}_4\text{O}_7\text{Ta}$
formula weight	1251.34	1514.04
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a [pm]	1313.3(2)	1941.8(2)
b [pm]	1621.0(2)	2032.1(2)
c [pm]	1651.0(2)	1993.1(2)
α [°]	86.70(5)	90.0
β [°]	74.38(5)	99.49(5)
γ [°]	71.19(5)	90.0
V (10^6 pm^3)	3202.5(7)	7756(1)
Z	2	4
$F(000)$ [e^-]	566	3112
$\mu(\text{Mo-K}_\alpha)$ [cm^{-1}]	17.3	30.0
cryst. size [mm]	$0.4 \times 0.3 \times 0.3 \text{ mm}$	$0.5 \times 0.2 \times 0.2 \text{ mm}$
T ($^\circ\text{C}$)	-153°C	-153°C
θ_{max}	$< 20^\circ$	$< 20^\circ$
hkl range	$\pm 13, 0/17, \pm 17$	$-18/-1, 0/19, -18/19$
collected reflections	6250	5370
unique reflections	5972	4263
R_{int}	0.06	0.4057
refined parameters	739	776
R_1/wR_2 (all data)	0.072/0.141	0.094/0.202
R_1/wR_2 [$I > 2\sigma(I)$]	0.054/0.128	0.068/0.182

intensities were measured using the ω -scan method with a maximum of 60-s measuring time per reflex, allowing 25% of the time for background measurement. After applying corrections for Lorentz polarization and Ψ -scan absorptions the structure was solved using the SHELX programs^[21]. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were fixed in calculated positions; a riding model was used for methyl and methylene hydrogen atoms. Details are listed in Table 2.

Heptakis(ether)tetralthium Tribromide Hexa-p-tolyltantalate(V): 320 mg (0.89 mmol) of TaCl₅ and 15 ml of dry pentane were heated at -65°C in a Schlenk tube equipped with a magnetic stirring bar. 1.77 ml (3.21 mol) of a 1.72 M solution of *p*-tolyl lithium in diethyl ether was added slowly. All further procedures were carried out in the dark. After stirring for 4 h at 70°C , a yellow solution and a green-grey deposit were formed. – After warming slowly to -30°C , the deposit turned brown and the solution red. Stirring at room temperature overnight, filtration of the deposit, washing with ether, and concentrating under vacuum gave a brown-yellow solution. Orange-yellow crystals formed from the solution when kept at -10°C .

A suitable crystal was selected, mounted on a diffractometer, and measured as described above. After DIFABS^[22] absorption correction, all atoms except hydrogen atoms and some solvent carbon atoms were refined anisotropically. The solvent carbon atoms were refined isotropically, and the hydrogen atoms were fixed in calculated positions. Methyl and methylene hydrogen atoms were located by use of a riding model. Further details of the single-crystal structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-100081 and -100152, the names of the author, and the journal citation.

^[1] V. Pfennig, K. Seppelt, *Science* **1996**, *271*, 626–628.

^[2] M. Kaupp, *J. Am. Chem. Soc.* **1996**, *118*, 3018–3024.

- ^[3] C. Landis, T. Cleveland, T. K. Firman, *J. Am. Chem. Soc.* **1995**, *117*, 1859–1860.
- ^[4] S. K. Kang, T. A. Albright, O. Eisenstein, *Inorg. Chem.* **1989**, *1989*, 1611–1613.
- ^[5] M. Shen, H. F. Schaefer III, H. Partridge, *J. Chem. Phys.* **1993**, *98*, 508–521.
- ^[6] S. K. Kang, H. Tang, T. A. Albright, *J. Am. Chem. Soc.* **1993**, *115*, 1971–1981.
- ^[7] P. M. Morse, G. S. Girolami, *J. Am. Chem. Soc.* **1989**, *111*, 4114–4116.
- ^[8] J. A. Labinger, *Comprehensive Organometallic Chemistry* (Ed.: G. Wilkinson), Pergamon Press, **1982**, p. 705–782; D. E. Wigley, S. D. Gray, *Comprehensive Organometallic Chemistry II* (Ed.: G. Wilkinson), Elsevier Science Ltd., **1995**.
- ^[9] C. Pulham, A. Haaland, A. Hammel, K. Rypdal, H. P. Verne, H. V. Volden, *Angew. Chem.* **1992**, *104*, 1534–1536; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1464–1466.
- ^[10] C. J. Piersol, R. D. Proffitt, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1993**, *12*, 1779–1783.
- ^[11] R. R. Schrock, P. Meanke, *J. Am. Chem. Soc.* **1974**, *96*, 5288–5290.
- ^[12] F. N. Tebbe (E. I. Dupont de Nemours and Co.) U.S. Patent 3,933,876, 1976.
- ^[13] L. J. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 6693–6700.
- ^[14] B. Sarry, V. Dobruskin, *J. Organomet. Chem.* **1968**, *13*, 1–8; *ibid.* *9–14*.
- ^[15] B. Sarry, P. Velling, *Z. Anorg. Allg. Chem.* **1976**, *426*, 107–112.
- ^[16] B. Sarry, R. Schaffernicht, *Z. Naturforsch.* **1981**, *86b*, 1238–1243.
- ^[17] R. Bartlett, P. P. Power, S. C. Shoncr, *J. Am. Chem. Soc.* **1988**, *110*, 1966–1968.
- ^[18] M. Minoura, T. Sagani, K. Akiba, C. Modrakowski, A. Sudau, K. Seppelt, S. Wallenhauer, *Angew. Chem.* **1996**, *108*, 2827–2829; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2660–2661.
- ^[19] S. Wallenhauer, D. Leopold, K. Seppelt, *Inorg. Chem.* **1993**, *32*, 3948–3951.
- ^[20] G. Brauer, *Handbuch der Präparativen Anorg. Chemie*, F. Encke Verlag, Stuttgart, **1971**, vol. 3, p. 1453.
- ^[21] G. Sheldrick, SHELXS, Program for Crystal Structure Solution, Göttingen 1986, and SHELXL 93, Program for Crystal Structure Refinement Göttingen, 1993.
- ^[22] N. Walker, D. Stuart, *Acta Cryst.* **1983**, *A39*, 158–166.

[96244]