Preparation and Structures of $[W(CH_3)_6]$, $[Re(CH_3)_6]$, $[Nb(CH_3)_6]^-$, and $[Ta(CH_3)_6]^-$

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Abstract: The results of the first crystal structure determination of $[W(CH_3)_6]$ are confirmed: its structure is strongly distorted towards a trigonal-prismatic C_{3v} symmetry, while $[Re(CH_3)_6]$ has a regular trigonal-prismatic symmetry, and $[Ta(CH_3)_6]^-$ and $[Nb(CH_3)_6]^-$ show a slight distortion from ideal trigonal prismatic. This distortion is similar but much weaker than that in $[W(CH_3)_6]$; the structure is additionally influenced by one strong $CH_3\cdots Li^+$ contact.

Keywords: hexamethyl complexes • structure elucidation • transition metals

Introduction

$[W(CH_3)_6]$ and $[Re(CH_3)_6]$, which were first synthesized by G. Wilkinson in 1973 and 1976, respectively,[1, 2] were always considered to be special cases of transition metal compounds because they are the only neutral hexamethylated species and they are quite unstable. Calculations which predicted that certain d^0 complexes should be nonoctahedral[3] and the experimental observation that $[Zr(CH_3)_6]^{2-}$ has an almost regular trigonal-prismatic structure,[4] (although cationic–anionic interactions could add to this peculiar structure), increased the general interest in these complexes with solely σ-bonding ligands. In subsequent years, a number of theoretical investigations were undertaken that have all shown that the compounds $[MH_6]$ and $[M(CH_3)_6]$ (M = transition metal) should indeed be nonoctahedral.[5–12] This discussion gained momentum when an electron diffraction study of $[W(CH_3)_6]$ in the gaseous state proved it to be trigonal-prismatic.[13] In 1996 we were able to obtain single crystals of $[W(CH_3)_6]$ and $[Re(CH_3)_6]$ by low-temperature crystallization (−90°) in acetone: we had found that recrystallization from carbohydrides resulted only in crystals which behaved very much like powder samples according to their X-ray diffraction patterns. The structural determination indicated a C_{3v}-distorted trigonal prism for $[W(CH_3)_6]$, which contains three longer W–C bonds with narrow angles, and three shorter bonds with wider angles.[14] We have also crystallized $[Re(CH_3)_6]$; it has a structure which is much closer to a regular trigonal prism.[14] Since these structures are of general interest, we now report some more detailed information, especially for $[Re(CH_3)_6]$, for which we chose the wrong space group in the original, previously reported determination.[14]

Since then, the important question has been as to whether there would be molecules or ions with similar irregular structures. We chose to start with the isoelectronic structures $[Ta(CH_3)_6]^-$ and $[Nb(CH_3)_6]^-$, for which no data has been published to date. Recently, we were able to crystallize and determine the structures of $[Ta(C_6H_5)_6]^-$ and $[Ta(4\text{-}CH_3C_6H_4)_6]^-$, which are close to trigonal prismatic, but show, of course, strong deviations from the ideal structure; this is due to the packing of the large ligand rings.[15]

Results and Discussion

The reactions between WF_6 or WCl_6 and $Zn(CH_3)_2$ are a convenient alternative for the preparation of $[W(CH_3)_6]$. There are several advantages over the original preparation from WCl_6 and $[Al(CH_3)_3]$; for example, the by-product ZnF_2 is completely insoluble in the solvents used, and no $(CH_3)_3N$ is required to trap the $[(CH_3)_2AlCl]_2$ generated as a by-product in the original preparation.

In the reaction between WF_6 and $Zn(CH_3)_2$, all members of the series $[F_xW(CH_3)_{6-x}]$ should be intermediates. We tried to monitor the reaction by ^{19}F NMR spectroscopy, since, in principle, it should be possible to identify all the $[F_xW(CH_3)_{6-x}]$ compounds, including the various possible isomers. However, these compounds with both substituents $[F_xW(CH_3)_{6-x}]$ only exist in minute amounts alongside WF_6 and $[W(CH_3)_6]$, and therefore are barely detectable, even by sensitive ^{19}F NMR spectroscopy. So the interesting questions remain unanswered: namely at which stage of methylation the change from octahedral (WF_6) to trigonal-prismatic and further to distorted trigonal-prismatic $[W(CH_3)_6]$ occurs, and

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whether some of these intermediates show fluxionality between several geometries. We were only able to identify $[F_5WCH_3]$ by its doublet–quintet ^{19}F NMR spectrum, which confirms that it has the same octahedral structure as WF_6 (Figure 1).

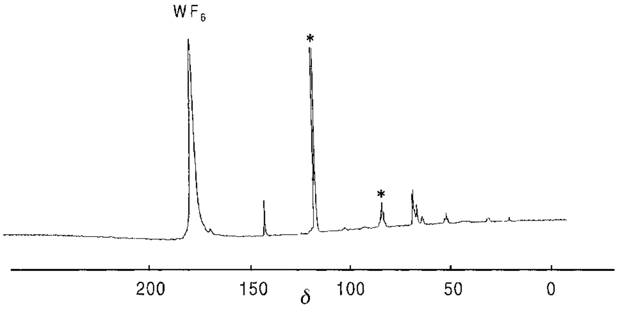

Figure 1. ^{19}F NMR spectrum of $[W(CH_3)_6]$ dissolved in WF_6 (20 °C, 376.3 MHz). The doublet–quintet system, denoted by (*), is due to $[F_5WCH_3]$.

We found that the crystallization of needle-shaped single crystals of $[W(CH_3)_6]$ from acetone at −90 °C is easily reproducible. We repeated the crystal structure analysis of $[W(CH_3)_6]$, which we have already published, not only because of its importance for the understanding of the general bonding principles in this compound, but also to see if it might crystallize in another manner (polymorphism) and also to check whether our original choice of space group was correct. We confirmed our previously published results, especially the occurrence of two crystallographically different molecules in the noncentrosymmetric orthorhombic lattice. Bond lengths and angles varied slightly, depending somewhat on the chosen crystal and the way the absorption correction was performed. Numerical values for the bond lengths and angles are taken from a data set which we believe to be the best one so far. The two crystallographically different molecules in the unit cell are packed slightly differently, as already discussed,[14] but both molecules are very much alike, having a C_{3v}-distorted trigonal-prismatic structure (Figure 2 and Table 1). Most of the hydrogen atoms can be located in difference Fourier maps, and there is no evidence so far for any agostic positioning of the hydrogen atoms. The C_{3v} distortion from a regular prismatic structure is such that the bond angles between the three shorter bonds are larger, while those between the three longer bonds are quite small. The average difference in bond length between the long and the short bonds is 8.5 pm or 4 %. The average bond length of the long bonds (av 218.7 pm) is between those of $[Ta(CH_3)_6]^-$ (222.6 pm, excluding the Ta–C bond lengthened by the Li^+ contact), and those of $[Re(CH_3)_6]$ (212.5 pm). Thus, the short bonds can be regarded as exceptional (av = 210.2 pm).

It is worth comparing the experimental structure with the results from the most sophisticated and most recent ab initio calculations:[12] W–C bond lengths and C-W-C bond angles are in very good agreement (Table 1). The calculations predict a very small rotation (a few degrees) of the methyl groups with retention of C_3 symmetry; this lowers the energy by 0.6–3.2 kJ mol^{-1} (depending on the way electron correlation was included in the calculation). The methyl groups also seem to be tilted slightly away from the direction of the W–C bond. This is interpreted in terms of in weak agostic bonding, especially of one of the hydrogen atoms situated on each of the methyl groups with shorter bonds. Of course, the crystal structure cannot address this question satisfactorily; however, the experimentally found orientation of the methyl groups, best seen in Figure 2 bottom, greatly resembles the calculated orientation.

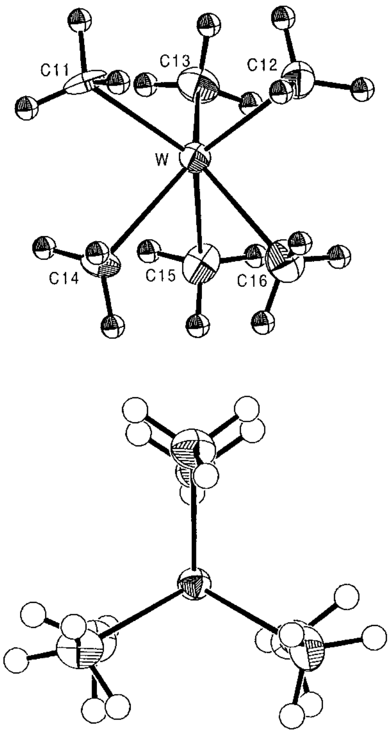

Figure 2. Ortep plot of $[W(CH_3)_6]$, molecule I, viewed from side (top) and top (bottom). The structure of molecule II is qualitatively the same; bond lengths and angles differ at most by 2 pm and 0.8°, respectively. For numerical values see Table 1.

Table 1. Results of the X-ray structural determination and the calculated structure of $[W(CH_3)_6]$: bond lengths [pm] and angles [°].[a]

Molecule I		Molecule II		Calculated	
W1–C11	210.1(11)	W2–C21	208.2(15)	W–C1	214.7
W1–C12	210.3(13)	W2–C22	210.2(14)		
W1–C13	211.8(14)	W2–C23	210.5(14)		
W1–C14	217.9(14)	W2–C24	217.7(11)	W–C4	220.9
W1–C15	219.8(14)	W2–C25	218.1(16)		
W1–C16	220.4(14)	W2–C26	218.3(14)		
C11-W1-C12	95.7(5)	C21-W2-C22	93.9(6)	C1-W-C2	95.6
C12-W1-C13	98.8(6)	C21-W2-C23	94.2(8)		
C12-W1-C13	96.4(6)	C22-W2-C23	96.0(6)		
C14-W1-C15	76.5(5)	C23-W2-C25	75.5(6)	C4-W-C5	75.6
C14-W1-C16	76.2(5)	C24-W2-C25	76.0(5)		
C15-W1-C16	75.3(5)	C25-W2-C22	75.7(7)		

[a] Ref. [12b], quasi-relativistic calculation.

The best method for the preparation of $[Re(CH_3)_6]$ is still the one from $[ReOCl_4]$ with excess $LiCH_3$ with the intermediate formation of $[Re(CH_3)_8]^{2-}$.[2] Again, needle-shaped single crystals were obtained from acetone at −90 °C. The results of the crystal structure analysis of $[Re(CH_3)_6]$ are given in Figure 3 and Table 2. We discovered that in the originally reported crystal structure we had chosen the wrong space group (*Cc* instead of $P2_1/n$), because all the reflections with $h+l \neq 2n$ were weak and had been overlooked. Luckily, this does not change the structure of the molecule very much. $[Re(CH_3)_6]$ is an almost perfect trigonal prism. Thus, it is evident that the addition of one electron to the $[W(CH_3)_6]$ system changes the structure from distorted trigonal prismatic to regular trigonal prismatic. The average Re–C bond length is 212.5 pm. This value is comparable with the value of 211.7 pm in $[ReO(CH_3)_4]$[16] and 206.0(9) pm in $[CH_3ReO_3]$[17]. The progression towards shorter bond lengths reflects the increasing unsaturation of the central atom. All hydrogen atoms, except one, could be located and refined, and there is no sign of any agostic positioning. However, X-ray diffraction is not the method of choice for settling this question.

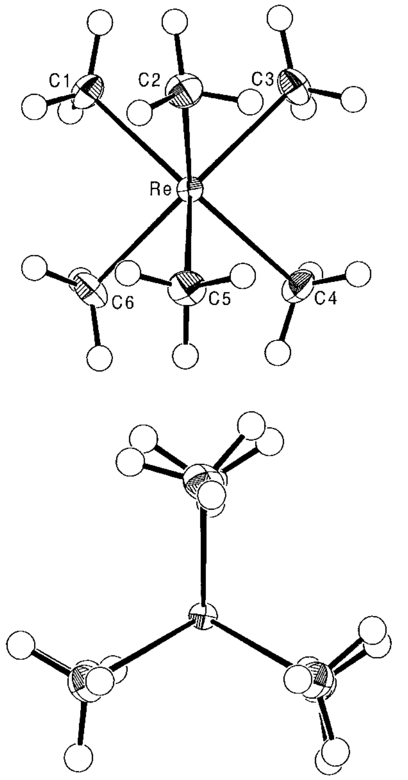

Figure 3. Ortep plot of $[Re(CH_3)_6]$, viewed from side (top) and top (bottom). For numerical values see Table 2.

Table 2. Results of the X-ray structural determination and the recent calculation of $[ReCH_3]$: bond lengths [pm] and angles [°].[a]

	X-ray	Calculated		X-ray	Calculated
Re1–C1	211.8(5)	215.1	C1-Re1-C2	82.8(2)	83.6
Re1–C2	212.8(5)		C1-Re1-C3	83.3(2)	
Re1–C3	213.7(6)		C2-Re1-C3	84.3(2)	
Re1–C4	213.2(5)		C4-Re1-C5	83.7(2)	
Re1–C5	213.0(5)		C4-Re1-C6	83.8(2)	
Re1–C6	212.2(5)		C5-Re1-C6	84.3(2)	

[a] ref [12b].

Finally, we want to address the question of how the regular trigonal-prismatic structure of $[Zr(CH_3)_6]^{2-}$, which is iso(valence)electronic to $[W(CH_3)_6]$, can be explained. In order to narrow down this question we have prepared, possibly for the first time, compounds containing the anions $[Nb(CH_3)_6]^-$ and $[Ta(CH_3)_6]^-$, and have also determined their crystal structures. The best method of preparation of $[Ta(CH_3)_6]^-$ is from $[Ta(CH_3)_5]$, obtained from TaF_5 and $LiCH_3$, which is treated with $LiCH_3$ to give $[Ta(CH_3)_6]^-$. Although it is difficult to handle pure $[Ta(CH_3)_5]$ because it is sensitive towards oxygen, moisture, and temperatures above −40 °C, this method is superior to the direct preparation of $[Ta(CH_3)_6]^-$ from TaF_5 because essentially no by-products are produced which could interfere in the difficult crystallization. $[Nb(CH_3)_6]^-$ was also obtained in two steps from NbF_5 and $LiCH_3$, but with the intermediate $[Nb(CH_3)_3F_2]$, mainly because handling $[Nb(CH_3)_5]$ in preparative amounts (>0.5 g) is dangerous because of the explosive nature of this material. The crystal structures of the compounds $[Li(OEt_2)_3]^+[Nb(CH_3)_6]^-$ and $[Li(OEt_2)_3]^+[Ta(CH_3)_6]^-$ are almost identical; it is possible that the two compounds are isomorphous. At first glance, both anions have a regular trigonal-prismatic structure, which is influenced by the contact of the Li^+ ion to one methyl group. This results in a lengthening of these particular Nb–C and Ta–C bonds and also affects the angles in a systematic manner, see Figures 3 and 4 and Table 3. If one considers the experimental C-Ta-C and C-Nb-C bond angles, one can detect also a C_{3v} distortion similar to that in $[W(CH_3)_6]$, which is slightly more pronounced in $[Nb(CH_3)_6^-]$ than in $[Ta(CH_3)_6]^-$: one triplet of methyl groups, namely the one which does not contain the methyl group that has a contact to Li^+, displays quite large angles (av Me-M-Me = 87.9° (M = Nb) and 86.3° (M = Ta)). However, the distortion of the bond angles by the contact to the Li^+ cation is also very effective. Bond lengths vary only slightly in these two triplets. This is in good agreement with calculations of $[Nb(CH_3)_6]^-$ (Table 3). Calculations predict that the energy minimum for $[Nb(CH_3)_6]^-$ should have a C_{3v}-distorted trigonal prism as in $[W(CH_3)_6]$, with a considerable distortion of the bond angles and lesser distortion of the bond lengths.[12] However, this structure is calculated to be only 0.8 kJ mol^{-1} below that of the regular

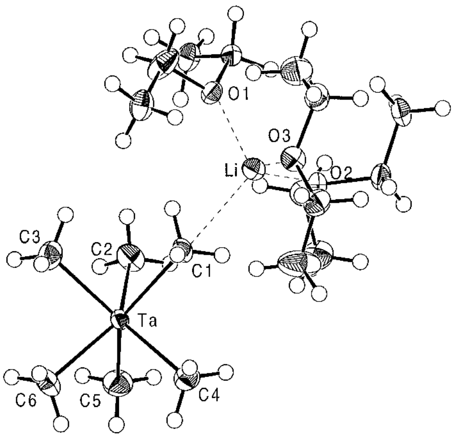

Figure 4. Ortep plot of one formula unit of $[Li(OEt_2)_3]^+[Ta(CH_3)_6]^-$. The structure of $[Li(OEt_2)_3]^+[Nb(CH_3)_6]^-$ is virtually identical (see Table 3).

Table 3. Results of the X-ray structural determination for comparison with the data obtained by calculation of $[Ta(CH_3)_6]^-$ and $[Nb(CH_3)_6]^-$ in $[Li(Et_2O)_3]^+[Ta(CH_3)_6]^-$ and $[Li(Et_2O)_3]^+[Nb(CH_3)_6]^-$. Bond lengths [pm] and angles [°].[a]

	X-ray	Calculated		X-ray	Calculated	
		D_{3h}			D_{3h}	C_{3v}
Ta1 – C1	226.2(4)	226.6	Nb – C1	225.8(6)	226.2	226.8
Ta1 – C2	220.7(4)		Nb – C2	222.5(7)		
Ta1 – C3	222.0(5)		Nb – C3	221.7(7)		
Ta1 – C4	222.4(5)		Nb – C4	220.5(7)		225.3
Ta1 – C5	222.7(4)		Nb – C5	222.5(7)		
Ta1 – C6	223.0(4)		Nb – C6	222.7(7)		
C1-Ta-C2	81.3(2)	84.8	C1-Nb-C2	80.0(3)	84.7	79.8
C1-Ta-C3	86.9(2)		C1-Nb-C3	80.7(3)		
C2-Ta-C3	81.7(2)		C2-Nb-C3	85.1(3)		
C4-Ta-C5	89.0(2)		C4-Nb-C5	90.9(3)		90.2
C4-Ta-C6	81.9(2)		C4-Nb-C6	89.9(3)		
C5-Ta-C6	88.2(2)		C5-Nb-C6	83.0(3)		

[a] Ref. [12b].

trigonal-prismatic structure. $[Ta(CH_3)_6]^-$ should have a regular trigonal-prismatic structure.

We interpret these results as a consequence of the negative charge in the anions, which is certainly delocalized among the six methyl groups. It lends enough interligand electrostatic repulsion so that the sterically highly unfavorable $[W(CH_3)_6]$ structure is no longer obtained, or the deviation is only weakly expressed.

The Ta – C bond lengths (av 222.6 pm, excluding the Ta – C bond lengthened by the Li^+ contact) can be compared to the apical Ta – C bond of 211(2) pm and the basal Ta – C bonds (218.0(5) pm in square-pyramidal $[Ta(CH_3)_5]$).[18] The lengthening caused by steric crowding and the addition of a negative charge is apparent. However, it must be kept in mind that the trigonal-prismatic structure of $[Ta(CH_3)_6]^-$ cannot be obtained by simply adding the sixth ligand to the basal plane of $[Ta(CH_3)_5]$. The $[Ta(CH_3)_6]^-$ structure is obtained by the addition of the sixth CH_3 ligand to any of the triangular planes of the $[Ta(CH_3)_5]$ square pyramid. This reaction pathway would require essentially only a shift of the apical methyl group away from the incoming methyl group with a simultaneous increase in its bond length. Bond lengths and angles of the basal methyl groups remain quite unaffected.

Conclusion

The search for other molecules or ions that have a $[W(CH_3)_6]$ structure should focus on the 4d period or positive ions, for example, the unknown $[Mo(CH_3)_6]$ and $[Re(CH_3)_6]^+$.[12]

Experimental Section

All experiments were carried out under pure, dry argon. Compounds stable at room temperature were handled in a glove box (concentration of O_2 and H_2O <1 ppm). Solvents were dried over sodium, degassed, and kept under argon. WF_6 was obtained from Merck Co. (Darmstadt, Germany). WCl_6 was made by chlorination of W metal at 600 °C.[19] $[Zn(CH_3)_2]$ (1M solution in heptane) was purchased from Aldrich Inorganic. TaF_5 and NbF_5 were obtained from Pennwalt Ozark – Mahoning Chemicals (Oklahoma USA) and sublimed in vacuo (180 °C, 10^{-3} mbar) before use. Solid methyllithium was obtained from the reaction of CH_3Cl with lithium in ether and double recrystallization, followed by drying in vacuo ($<10^{-4}$ mbar and 120 °C) which gave a white solid. Methyllithium solution in ether (1.6M) is commercially available (Sigma-Aldrich).

$[W(CH_3)_6]$:

From WCl_6: In a glove box WCl_6 (0.95 g, 2.4 mmol) was weighed into a glass container (50 mL) with two openings. *n*-Pentane (10 mL) was condensed in vacuo onto the WCl_6. A solution of $(CH_3)_2Zn$ in *n*-heptane (7 mL, 1M) was slowly added dropwise at – 78 °C. The reaction mixture was stirred for two days at – 35 °C. During this time the color turned deep orange. The mixture was filtered at – 10 °C and then concentrated in vacuo at – 70 °C. The yield (46 %) of $[W(CH_3)_6]$ was determined by its quantitative reaction with NO and by weighing the product $[(CH_3)_4W\{ON(CH_3)NO\}_2]$.[1]

From WF_6: A glass container (50 mL) with two openings was attached to a vacuum line, and WF_6 (1.1 g, 3.69 mol) and *n*-pentane (10 mL) were condensed into it in vacuo and with cooling (liquid nitrogen). A solution of $(CH_3)_2Zn$ in *n*-heptane (11.5 mL, 1M) was slowly added dropwise at – 78 °C. The mixture was stirred at – 35 °C for two days, filtered at – 10 °C, and concentrated in vacuo at – 70 °C to afford an orange solution. The yield (53 %) was determined as described above. ^1H NMR (CD_2Cl_2, – 20 °C, 400 MHz): $\delta = 1.72$ ($J(^{187}W,^1H) = 6.0$ Hz); $\{^1H\}^{13}C$ NMR (CD_2Cl_2, – 20 °C, 100,4 MHz): $\delta = 83.46$ ($J(^{187}W,^{13}C) = 43.2$ Hz).

Crystals were obtained by complete evaporation of the solvent mixture at – 70 °C in vacuo, and redissolution in acetone at – 60 °C. Slow cooling to – 90 °C gave needle-shaped, red-brown crystals.

$[Re(CH_3)_6]$: In a glove box, $ReOCl_4$ (0.5 g, 1.48 mmol) was weighed into a glass container with two openings, and Et_2O (10 mL) was condensed onto it. Under stirring, CH_3Li (15 mmol, 1.6M in Et_2O) was added dropwise at – 78 °C. The reaction mixture was allowed to warm slowly to room temperature for a few minutes, cooled quickly to – 50 °C, and then the solvent was pumped off. At – 78 °C, *n*-pentane (20 mL) and degassed H_2O (4 mL) were condensed onto the brown solid. CH_4 evolved as the mixture was allowed to warm to room temperature, and the pentane solution turned green. The solution was transferred into a glass ampoule by means of a 2 mm Teflon tube, the solvent was slowly pumped off at – 78 °C, and acetone was added. The residue was redissolved in acetone and cooled to – 95 °C to afford needle-shaped, dark green crystals.

$[Li(OEt_2)_3]^+[Ta(CH_3)_6]^-$: In a Schlenk tube (100 mL) equipped with a magnetic stirring bar, a suspension of $[TaF_5]$ (1.0 g, 3.6 mmol) in pentane (20 mL) was cooled to – 78 °C. Solid $LiCH_3$(0.35 g, 16 mmol) was added over a period of ≈30 min. The mixture was allowed to warm slowly to – 25 °C and then stirred for 16 h. The resulting light yellow solution containing a small amount of a brown deposit was distilled in vacuo and collected in a trap cooled by liquid nitrogen. After the mixture had been pumped for 16 h under vacuum ($p < 10^{-4}$ mbar), the Schlenk tube was allowed to warm to room temperature; the nonvolatile solid had turned black. Yellow, crystalline $[Ta(CH_3)_5]$ was found separately from the distilled solvent in the trap. It was redissolved in pentane at – 78 °C under argon to give a light yellow solution of $[Ta(CH_3)_5]$. This solution was concentrated under vacuum to 50 % and transferred into a small Schlenk tube (16 mm diameter, 300 mm long) by means of a Teflon tube. After addition of a small amount of ether (≈25 % excess) the solution was titrated with a solution of $LiCH_3$ in ether (1.6M) until it became a white suspension. The mixture was warmed to – 20 °C and then treated in a supersonic bath to give a very light yellow solution with a small amount of a white solid. Light yellow crystals were obtained from this solution on gradual cooling to – 90 °C.

$[Li(OEt_2)_3]^+[Nb(CH_3)_6]^-$: In a Schlenk tube (100 mL) equipped with a magnetic stirring bar, a suspension of $[NbF_5]$ (1.6 g, 8.5 mmol) in pentane/ether (1:1, 20 mL) was cooled to – 35 °C. A solution of $LiCH_3$ (10.6 mL, 17 mmol, 1.6M) in ether was added slowly. The mixture was stirred for 3 h, and then all volatiles of the resulting yellow suspension were distilled in vacuo into a trap cooled to – 78 °C. The Schlenk tube was allowed to warm to room temperature and pumped for 16 h ($p < 10^{-4}$ mbar). A yellow solid (presumably $[(CH_3)_3NbF_2]$), and part of the solvent were found in the trap, while the residue in the Schlenk tube had turned black. The yellow solid was redissolved in the distilled solvent and the resulting the yellow solution was transferred under argon into a small Schlenk tube by means of a Teflon tube. The mixture was titrated with a solution of $LiCH_3$ in ether (1.6M) until a white solid formed. After 2 h sedimentation, a clear yellow solution appeared above a gray solid. The liquid phase was transferred by means of a thin Teflon tube into an ampoule (10 mm). Yellow crystals precipitated from the solution when it was kept at $-90\,^{\circ}$C for a few days. Raman ($-80\,^{\circ}$C): $\tilde{\nu} = 2976$ (20, 2930 (35), 288 (30), 1445 (20), 1404 (12), 1327 (4), 1282 (3), 1139 (45), 1102 (55), 1063 (45), 1021 (5), 1000 (6), 912 (6), 898 (5), 835 (20), 795 (7), 784 (7), 616 (4), 492 (100), 405 (20), 316 (10) cm^{-1}.

Table 4. Crystallographic data.

	$[W(CH_3)_6]$	$[Re(CH_3)_6]$	$[Li(Et_2O)_3]^+[Ta(CH_3)_6]^-$	$[Li(Et_2O)_3]^+[Nb(CH_3)_6]^-$
M_c	274.05	276.41	500.45	412.41
T [°C]	-163	-163	-153	-153
space group	$Pbc2_1$(No. 29)	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a [pm]	630.9(1)	1114.6(3)	1054.2(1)	1054.2(1)
b [pm]	1315.8(1)	626.4(2)	1448.5(1)	1628.6(1)
c [pm]	2091.3(3)	1332.9(2)	1628.6(1)	1448.5(1)
β [°]	90	113.98(2)	90	90
V [10 pm^3]	1736.1(4)	850.3(4)	2487(2)	2486(3)
Z	8	4	4	4
absorption coeff [mm^{-1}]	13.22	14.2	4.43	0.493
θmax [°]	30	35	30	25
reflections collected	6492	2410	5923	2902
reflections, independent	5776	1725	5923	2902
refined parameters	165	120	229	220
R	0.048	0.021	0.026	0.041
$wR2$	0.109	0.053	0.069	0.117

Crystal structure determinations: (See also Table 4). Glass tubes containing single crystals were opened into the mouth of a special apparatus designed for handling moisture-, oxygen-, and temperature-sensitive compounds.[20] A suitable crystal was selected. In the case of $[W(CH_3)_6]$ and $[Re(CH_3)_6]$, the needle-shaped crystals were cut so that the maximum length did not exceed 1 mm in order to weaken the anisotropy of absorption. The crystal was mounted on a glass tip with perfluoropolyether ($[W(CH_3)_6]$, $[Re(CH_3)_6]$) or Nujol/methylcyclohexane ($[Nb(CH_3)_6]^-$ and $[Ta(CH_3)_6]^-$), and adjusted. The reflections were measured on a Enraf–Nonius CAD4 diffractometer with $Mo_{K\alpha}$ radiation and a graphite monochromator. Cell dimensions were obtained by fine orientation of 25 reflections with $20 < \theta < 25^{\circ}$. Data were collected in the ω-scan mode with a maximum of 60 s for each reflection, depending on intensity, and leaving 25% of the measuring time for background measurements. Friedel pairs were measured in case of the three noncentrosymmetric crystal systems. After Lorentz polarization and psi-scan absorption correction the structures were solved with the SHELX86 program[21] and refined with SHELXS97.[22] All atoms, except hydrogen, were refined anisotropically. $[W(CH_3)_6]$: Best results were obtained for a racemic twin of the noncentrosymmetric space group with occupational factors close to 50%. Since only most, but not all, hydrogen atoms could be located and refined, we chose a rigid methyl group refinement which allows the methyl groups to rotate and tilt against the W–C bonds. All hydrogen atoms were refined with a single, common isotropic vibrational parameter. $[Re(CH_3)_6]$: All hydrogen atoms, except one, could be refined independently with a single, common isotropic vibrational parameter. One hydrogen atom was found at a distance of 50 pm from the C6 atom. Therefore, the same rigid group refinement procedure as used for $[W(CH_3)_6]$ was applied which allowed rotation and tilting against the Re–C axes. $[Li(OEt_2)_3]^+[Ta(CH_3)_6]^-$: The hydrogen atoms on C1 (bridging between Ta and Li) were refined independently. All other hydrogen atoms were refined with rigid methyl and methylene groups. $[Li(OEt_2)_3]^+[Nb(CH_3)_6]^-$: All hydrogen atoms were refined with rigid methyl and methylene groups. 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-101029. 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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