*p-t*Bu groups and two THF molecules are disordered. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-130277. 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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Charting No-Man's Land in d^0 Transition Metal Six-Coordination: Structure Predictions for the Complexes [WCl$_5$CH$_3$], [WCl$_4$(CH$_3$)$_2$], and [WCl$_3$(CH$_3$)$_3$]**

Martin Kaupp*

Among the growing number of early, high-valent transition metal complexes that defy the traditional structural rules, the computationally predicted[1–3] and experimentally confirmed[4] distorted trigonal-prismatic structure of hexamethyltungsten, [W(CH$_3$)$_6$], holds a central role. Related, more ionic d^0 complexes such as [Zr(CH$_3$)$_6$]$^{2-}$ or [Ta(CH$_3$)$_6$]$^-$ have regular trigonal-prismatic structures.[2c, 4b, 5] In contrast to these fascinating compounds, the majority of hexacoordinate d^0 systems are octahedral, such as the Group 6 hexahalides.[3, 6] A major difference[1, 3, 7] between these two sets of complexes is that cylindrical π-donor halide (or related) ligands favor the octahedron, whereas exclusively σ-bonding ligands prefer nonoctahedral arrangements (the latter preference can be rationalized within relatively simple valence bond[2a, 8] or molecular orbital[1, 2b,c, 3, 7, 9] frameworks). We are thus facing two seemingly very different structural paradigms within closely related series of compounds. This suggests that one should be able to find complexes with preferences *between* octahedral and distorted or regular trigonal-prismatic structures. There are different routes into this "no-man's land". One route consists of replacing the cylindrical halide π-donor ligands by effectively single-faced π donors, for example as in thiolate complexes. This leads into the large and interesting field of dithiolene, dithiolate, and related complexes, the trigonal twist angles of which do indeed cover a large range between octahedral and trigonal prismatic,[10] depending on bond polarity and on the actual π-donor abilities of the ligands. Herein are reported the first computational results along a different route into this intermediate region, on which practically nothing has been known: Starting from octahedral WCl$_6$ complexes, we replace successively π-donor chloride ligands by σ-donor methyl groups. Structural predictions for the first three members of this [WCl$_{6-n}$(CH$_3$)$_n$] series (n = 1–3) and for the fluoride complex [WF$_5$CH$_3$] are made.

Figure 1 shows the most important stationary points computed at the gradient-corrected density functional theory (DFT) level[11] for [WCl$_5$CH$_3$] (**1**). We note that this complex has been prepared and was characterized by IR and ^{1}H NMR spectroscopy,[12] but nothing is known about its structure. The

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Supporting information for this article (one Figure with computed IR spectra for [WCl$_5$CH$_3$]) is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

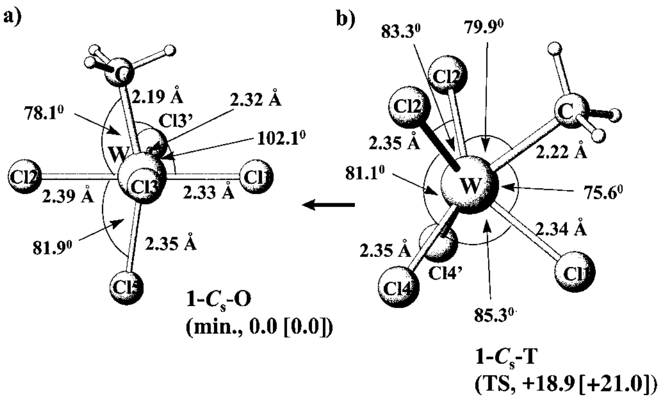

Figure 1. DFT-optimized stationary points for $[WCl_5CH_3]$ (**1**). Relative energies in $kJ\,mol^{-1}$ (values in brackets include zero-point vibrational energy corrections). a) Distorted octahedral minimum (**1-*C*$_s$-O**), further angles [°]: Cl1-W-Cl5 97.9, Cl1-W-Cl2 179.8, Cl3-W-Cl3′ 166.3, Cl1-W-Cl3 87.0; b) trigonal-prismatic transition state (**1-*C*$_s$-T**).

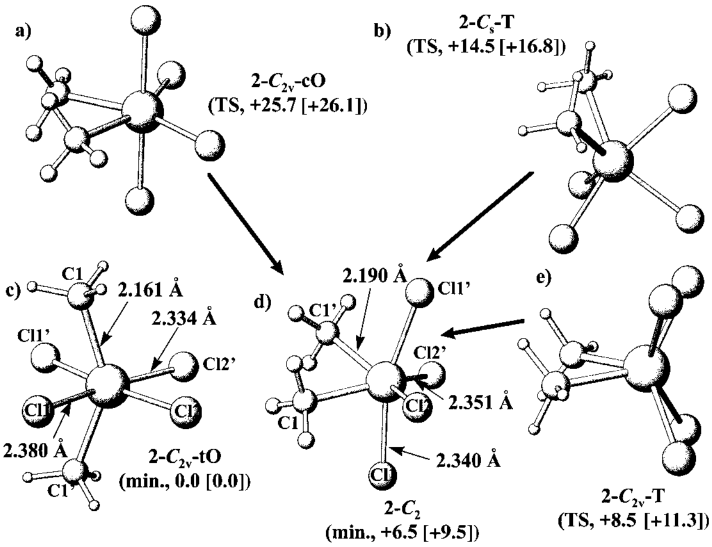

Figure 2. DFT-optimized stationary points for $[WCl_4(CH_3)_2]$ (**2**). Relative energies in $kJ\,mol^{-1}$ (values in brackets include zero-point vibrational energy corrections). a) **2-*C*$_{2v}$-cO**; b) **2-*C*$_s$-T**; c) **2-*C*$_{2v}$-tO**. Angles [°]: C1-W-C1′ 144.0, C1-W-Cl1 78.9, C1-W-Cl2 103.2, Cl1-W-Cl1′ 102.8, Cl2-W-Cl2′ 84.6, Cl1-W-Cl2 86.3; d) **2-*C*$_2$**. Angles [°]: C1-W-C1′ 73.4, C1-W-Cl1 82.0, C1-W-Cl1′ 113.4, Cl1-W-Cl1′ 161.5, Cl2-W-Cl2′ 130.9, Cl1-W-Cl2 88.9, Cl1-W-Cl2′ 83.4; e) **2-*C*$_{2v}$-T**.

calculations give a distorted octahedral C_s-symmetrical minimum energy structure (**1-*C*$_s$-O**, Figure 1 a). The methyl group and its *trans* chloride ligand are bent characteristically towards one of the *cis* ligands. This leads to a moderate energy gain relative to a C_{4v} heavy-atom skeleton (by ca. $7\,kJ\,mol^{-1}$) and is shown by population analyses to be due to slightly improved W–C bonding.[13] A configuration with the methyl group bisecting the angle between two *cis* ligands is energetically almost indistinguishable (but has a small imaginary vibrational frequency of about $i17\,cm^{-1}$ at this level), and we conclude that the tilted methyl group and its *trans* chloride ligand may rotate essentially without barrier above the plane of the *cis* ligands. A trigonal-prismatic structure, also with C_s symmetry (**1-*C*$_s$-T**, Figure 1 b), is characterized as a low-lying transition state (TS), only about $20\,kJ\,mol^{-1}$ above the distorted octahedral minimum. This is remarkable considering that we compute at the same theoretical level a D_{3h} TS for WCl_6 to be about $80\,kJ\,mol^{-1}$ above the octahedral minimum. Thus, the introduction of one methyl group leads already to drastic changes in the structural behavior, and to a compound that may be considered fluxional at room temperature. Population analyses show that this behavior is due to a delicate balance between maximization of W–C σ bonding (which is most covalent in **1-*C*$_s$-T**), as well as maximization of W–Cl π bonding and minimization of ligand repulsion (both favored in an octahedral arrangement). Our computed IR spectra for **1-*C*$_s$-O** and **1-*C*$_s$-T** (Figure S1 in Supporting Information) agree well with the experimental data but are not diagnostic with respect to the structure. Similarly, the ^1H chemical shifts are not helpful in this respect.

Introducing the second methyl group in $[WCl_4(CH_3)_2]$ leads to the possibility of various isomeric structures; Figure 2 summarizes only the most important stationary points located on the potential energy surface. The relations between the stationary points may be described roughly by rotations of opposite trigonal faces from distorted trigonal antiprismatic (distorted octahedral) to trigonal-prismatic arrangements (see fat arrows in Figure 2; details of these transformations are presently being explored). We have found two minima. One is a *trans*-octahedral C_{2v}-symmetrical structure (**2-*C*$_{2v}$-tO**), the other is a C_2 structure (**2-*C*$_2$**), which lies about $10\,kJ\,mol^{-1}$ higher in energy (including zero-point vibrations). This latter minimum **2-*C*$_2$** is very interesting, as its coordination arrangement is not uniquely characterizable as an octahedron or prism. It is somewhat closer to **2-*C*$_{2v}$-T**, a trigonal-prismatic TS with the two methyl groups in opposite trigonal faces but in an eclipsed position, than to the *cis*-octahedral **2-*C*$_{2v}$-cO** TS, which is already about $26\,kJ\,mol^{-1}$ higher in energy. The **2-*C*$_{2v}$-tO** minimum is again characteristically distorted, like the minimum **1-*C*$_s$-O** of $[WCl_5CH_3]$ (see Figure 1), and for similar reasons. Another trigonal-prismatic TS, **2-*C*$_s$-T**, is connected to **2-*C*$_2$** by rotation of a $W(CH_3)_2Cl$ face. The TS that connects **2-*C*$_{2v}$-tO** with **2-*C*$_2$** has not yet been located but is expected to be also at low energy. We conclude that the energy differences between octahedral and prismatic structures have essentially vanished already at this point, and we suspect the system to be highly fluxional.

Introducing the third methyl group in $[WCl_3(CH_3)_3]$ changes the picture again significantly (Figure 3). Now the only minima found are the two trigonal-prismatic isomers **3-*C*$_1$-T** and **3-*C*$_3$-T**, of which the latter has all three methyl groups in the same trigonal face and appears to be very slightly higher in energy. Structures **3-*C*$_s$-O** and **3-*C*$_{3v}$-O** derived from meridional and facial octahedra, respectively, are only transition states. While the former is still at moderate energy, the latter is not competitive. Thus, the trigonal prism is already notably more favorable than an octahedral coordination for $[WCl_3(CH_3)_3]$. We note for comparison that for $[W(CH_3)_6]$ at the same computational level,[1b,c] a distorted octahedral C_{3v}-structure analogous to **3-*C*$_{3v}$-O** is already about $132\,kJ\,mol^{-1}$ above the distorted trigonal-prismatic C_3 symmetrical minimum structure (which is analogous to **3-*C*$_3$-T**). Thus, octahedral arrangements become even less favorable upon substitution of the remaining three chloride ligands by

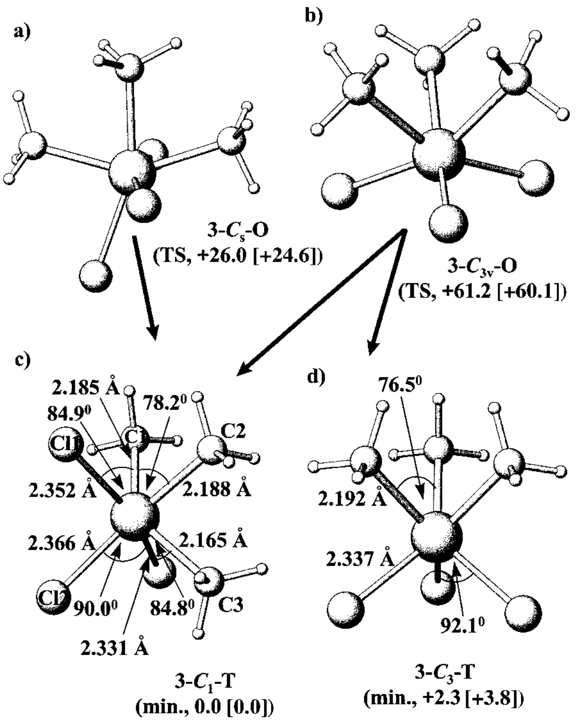

Figure 3. DFT-optimized stationary points for [WCl$_3$(CH$_3$)$_3$] (**3**). Relative energies in kJ mol^{-1} (values in brackets include zero-point vibrational energy corrections). a) **3-C_s-O**; b) **3-C_{3v}-O**; c) **3-C_1-T**, further angles [°]: Cl1-W-C2 80.2, Cl2-W-C2 87.7; d) **3-C_3-T**.

methyl groups, as one might expect from the interplay between σ- and π-donor ligands.

At the theoretical level used here, we compute the trigonal prism to be only about 43 kJ mol^{-1} above the octahedron for WF$_6$ compared to about 80 kJ mol^{-1} for WCl$_6$. This is due to the weaker π-donor character of the fluoride ligands (it cannot be due to ligand repulsion, as the latter would favor the octahedron more strongly for WF$_6$), as confirmed by our bonding analyses. The trigonal prism should thus become competitive even earlier along our substitution pathway for the [WF$_{6-n}$(CH$_3$)$_n$] series. Indeed, our first calculations confirm that for [WF$_5$CH$_3$], the trigonal-prismatic structure (cf. **1-C_s-T** in Figure 1) is a minimum at this theoretical level, already 2 kJ mol^{-1} below the best distorted octahedral arrangement. Kleinhenz et al.[4b] assigned two peaks in the ^{19}F NMR spectra obtained when dissolving [W(CH$_3$)$_6$] in WF$_6$ to [WF$_5$CH$_3$]. From the doublet and quintet character of the high-frequency and low-frequency peaks, respectively, they concluded that the structure is octahedral. Obviously, our calculations are not consistent with a rigid octahedral structure for the free complex.[14] However, in view of the very small energy differences involved, we cannot exclude the stabilization of a regular structure in the environment of the WF$_6$ matrix. Similar structural behavior as for the analogous chloro complexes is also indicated by our calculations for [WF$_4$(CH$_3$)$_2$] and [WF$_3$(CH$_3$)$_3$],[15] with a somewhat larger preference for arrangements derived from a trigonal prism.

While there is experimental evidence for the existence of the monosubstituted complexes [WX$_5$CH$_3$] (X = F, Cl),[4b, 12] no indications for multiply methyl-substituted complexes have been seen. Our preliminary calculations of isodesmic reaction energies indicate that thermodynamically the mixed compounds are more stable than the sum of the homoleptic complexes. Also, reactions such as that in Equation (1) are

$$[WX_5CH_3] + [W(CH_3)_6] \rightarrow [WX_4(CH_3)_2] + [WX(CH_3)_5] \tag{1}$$

computed to be exothermic (by −31 and −44 kJ mol^{-1} for X = Cl, F, respectively, including zero-point vibrational energy corrections) and should also be favored entropically. It appears that kinetic rather than thermodynamic factors limit the access to these complexes. Reductive elimination reactions will of course have to be considered. We are presently studying systematically the entire range of heteroleptic complexes [WX$_{6-n}$(CH$_3$)$_n$] (n = 1–5; X = F, Cl) by quantum chemical methods.[15] This includes predictions of spectroscopic parameters that may help to experimentally characterize these species, once they have been prepared.

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Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, **1995**; d) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123; e) A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431; f) T. H. Dunning, H. Hay in *Methods of Electronic Structure Theory*; *Modern Theoretical Chemistry*, *Vol. 3* (Ed.: H. F. Schaefer III), Plenum, New York, **1977**.

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[13] Related distortions have been discussed for complexes such as $[TiCl_3RL_2]$ ($R = CH_3$, C_2H_5; L_2 = diphosphane ligand),[7a] or $[MCl(OAr)_2H_2L]$ (M = Nb, Ta) (J. R. Clark, A. L. Pulvirenti, P. E. Fanwick, M. Sigalas, O. Eisenstein, I. P. Rothwell, *Inorg. Chem.* **1997**, *36*, 3623). For related distortions in heteroleptic five-coordinate complexes, see: T. R. Ward, H.-B. Bürgi, F. Gillardoni, J. Weber, *J. Am. Chem. Soc.* **1997**, *119*, 11974; M. Kaupp, *Chem. Eur. J.* **1998**, *4*, 2059.

[14] Preliminary DFT calculations of ^{19}F shifts give surprisingly poor agreement with experiment and let us suspect the presence of significant intermolecular interactions in the WF_6 solutions.

[15] M. Kaupp, unpublished results.

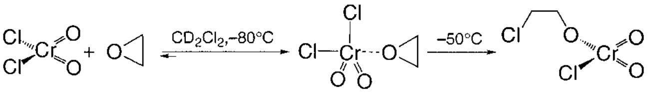
Trapping of an Organic Radical by an $O{=}Cr^{VI}$ Function**

Tobias Wistuba, Christian Limberg,* and Peter Kircher

Dedicated to Professor Helmut Werner
on the occasion of his 65th birthday

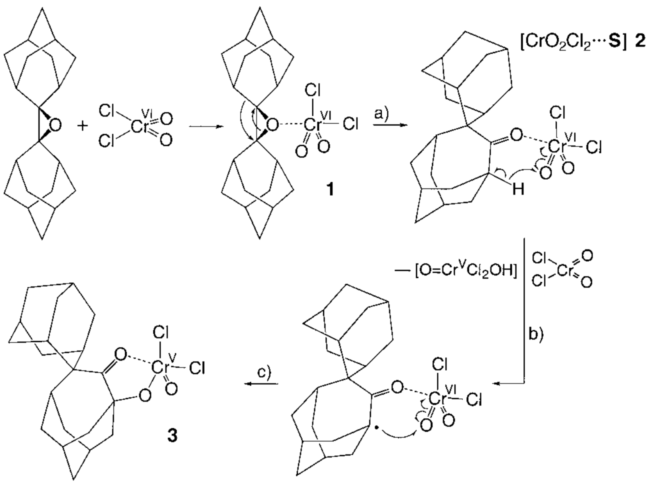
Traditionally H-atom transfer onto metal oxo species in nature and technology was rationalized based on an analogy with organic radical chemistry, that is unpaired electron density was thought to be transferred to the oxygen atoms of the metal compounds, which are then ready to undergo radical reactions.[1] In the meantime it has been established that d^0-metal oxo systems (thus systems without unpaired spin density) can abstract hydrogen atoms from saturated organic systems, and a progression has occurred from thinking about radicals and spin density to an approach based on the thermochemistry of the H-atom transfer step.[2] Furthermore from the results of kinetic studies and radiolysis experiments it has been inferred that the M=O functions (M = metal) of d^0-metal oxo compounds such as CrO_2Cl_2,[3] CrO_4^{2-},[4] and MnO_4^-[2, 4] are also capable of trapping organic radicals. For instance the radicals resulting from the H-abstraction step in oxidations of aliphatic compounds with CrO_2Cl_2 were proposed to add to Cr=O groups of excess CrO_2Cl_2 to yield Cr^V alkoxides, which then release the alcohols found among the oxidation products after aqueous workup. Here we provide evidence for this type of reactivity for the first time through the isolation of such a Cr^V primary intermediate.

Examining Cr^{VI} alkoxides[5] produced by epoxide cleavage with CrO_2Cl_2 (Scheme 1), we noticed their strong tendency to decompose[6] by α-proton-coupled electron transfers onto the Cr=O functions, yielding paramagnetic complexes of chlorinated carbonyl compounds.[5] To prepare stable $[Cl(O)_2Cr(OCR_2CR_2Cl)]$ derivatives we therefore set out by employing epoxides that lack α-H atoms. Brought into contact with CrO_2Cl_2, tetramethyl- and tetraphenyloxirane, however, isomerized to the corresponding ketones already at very low temperatures, while epoxides like perfluoropropene oxide were too electron poor to react at all. Hence the ideal epoxide substrate should be fully substituted at the α-position, electron-rich, and not prone to rearrangements.



Scheme 1. Oxirane cleavage with CrO_2Cl_2.

Bisadamantylidene epoxide (BAE) fulfils these requirements, and thus its reaction with CrO_2Cl_2 was studied by NMR spectroscopy at −50 °C. The ^{13}C NMR resonance for the epoxide ring carbon atoms of BAE were shifted by $\Delta\delta = 0.5$ to lower field, indicating the formation of a complex $[CrO_2Cl_2 \cdot BAE]$ (**1**) (Scheme 2). However, comparing the shift difference found for oxirane (Scheme 1) on complexation ($\Delta\delta = 9.6$) it has to be concluded that—probably as a result of its steric bulk—BAE is comparatively weakly complexed by the Cr center.



Scheme 2. Proposed mechanism for the formation of **3**.

As we had hoped, the incorporation of the epoxide function into the adamantane framework prevented the epoxide/ketone isomerization within **1** quite effectively up to a temperature of −5 °C, but a formal Cr–Cl bond insertion of

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