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[13] Related distortions have been discussed for complexes such as [TiCl$_3$RL$_2$] (R = CH$_3$, C$_2$H$_5$; L$_2$ = diphosphane ligand),[7a] or [MCl(OAr)$_2$H$_2$L] (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.

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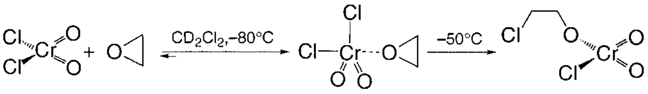
Trapping of an Organic Radical by an O=Cr^{VI} Function**

Tobias Wistuba, Christian Limberg,* and Peter Kircher

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

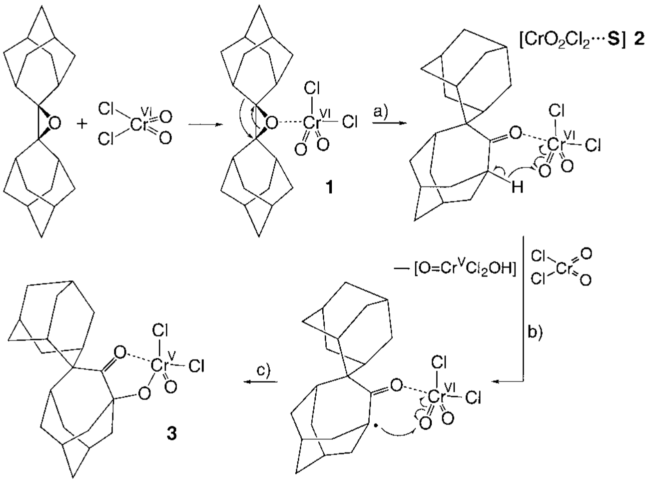
Traditionally H-atom transfer onto metal oxo species in nature and technology was rationalized based on an analogy with organic radical chemistry, that is unpaired electron density was thought to be transferred to the oxygen atoms of the metal compounds, which are then ready to undergo radical reactions.[1] 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$_2$Cl$_2$,[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$_2$Cl$_2$ were proposed to add to Cr=O groups of excess CrO$_2$Cl$_2$ 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$_2$Cl$_2$ (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)$_2$Cr(OCR$_2$CR$_2$Cl)] derivatives we therefore set out by employing epoxides that lack α-H atoms. Brought into contact with CrO$_2$Cl$_2$, 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$_2$Cl$_2$.

Bisadamantylidene epoxide (BAE) fulfils these requirements, and thus its reaction with CrO$_2$Cl$_2$ 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$_2$Cl$_2$·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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the epoxide failed to occur, too. However, further warming led to the formation of a paramagnetic main product, **3**, which could be crystallized when the reaction was performed on a preparative scale. A single-crystal X-ray analysis[7] (Figure 1) identified **3** as dichlorooxo((η^1,η^1)-spiro(adamantane-2,2′-homoadamantan-3-on-4-oate)chromate(v). The coordination sphere of its chromium center can be described as distorted trigonal bipyramidal with Cl2 and O2 as axial ligands (the O2-Cr-Cl2 angle is 164.88(3)°). Consequently, the Cl1-Cr-Cl2 angle of 93.35(3)° approximates a right angle, while O3-Cr-Cl1 is close to 120° (125.80(6)°). Compound **3** displays an ESR signal typical for d^1-Cr systems and to our knowledge it is the first structurally characterized neutral O=Cr^V alkoxide. However, the structures of a few charged species are known[8] and can serve for comparison. All bond lengths in **3** appear to lie within characteristic regions, that is they are very similar, for instance, to those found in [OCr(O$_2$CCOMeEt)$_2$]$^-$ (where $^-$O$_2$CC(OH)MeEt = 2-hydroxy-2-methylbutyrate).[8a]

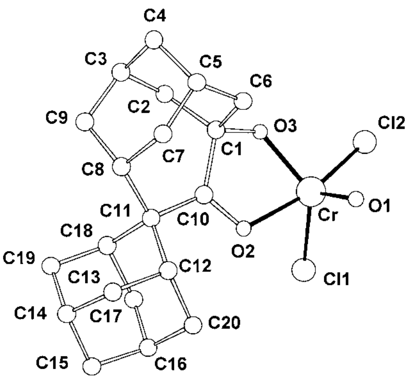

Figure 1. Molecular structure of **3**; all hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr–O1 1.561(2), Cr–O2 2.032(2), Cr–O3 1.781(2), Cr–Cl1 2.1991(8), Cr–Cl2 2.2139(7), C1–O3 1.432(2), O2–C10 1.240(2), C1–C10 1.527(3); O2-Cr-O3 78.83(6), O2-Cr-Cl2 164.77(5), Cl1-Cr-Cl2 93.35(3), O1-Cr-O2 93.09(7), Cr-O3-C1 120.1(1).

The formation of **3** is of particular interest and it can be rationalized by the mechanism shown in Scheme 2. The first step (a) consists of a Cr^{VI}-catalyzed epoxide/ketone isomerization that yields a spiro(adamantane-2,2′-homoadamantan-3-one) (**S**),[9] which remains coordinated at the Cr center to give **2**. In the next step (b) an α-H atom is selectively abstracted leading to a radical. In principle this could be envisaged to occur in the form of an intracomplex reaction or bimolecular reaction of **2** with free CrO$_2$Cl$_2$: the latter is known to be very selective in C–H activations,[3] and in fact there is some evidence for a preference with respect to the α-keto positions in certain systems.[3] However, the abstraction rates found so far were—even at 70 °C—comparatively low, and correspondingly we found that a reaction of the type as shown in Scheme 2 proceeds only to an insignificant extent when for instance CH$_3$C(O)CH(CH$_3$)$_2$ is employed under our conditions (0 °C). If on the other hand the spiro-ketone **S** is treated with CrO$_2$Cl$_2$ *directly*, that is if the investigation is started from **2** rather than **1**, the formation of paramagnetic centers can be detected already at temperatures below −50 °C, so that in the reaction of BAE the formation of **2** (step a in Scheme 2) must be rate-determining. Both the site-selectivity[10] and the high rate of the abstraction step (step b) can only be explained by a chelation-assisted intracomplex reaction—that is by a positioning of the α-H-atom directly beside a Cr=O group within **2** (compare the density functional theory (DFT)-optimized structure of **2** in Figure 2), so that the system sets out already at a relatively high level of the C–H activation barrier. After the abstraction, Cr(OH)(O)Cl$_2$ formed initially, indicating an inefficient radical trap.[3] However, it was rapidly exchanged by excess CrO$_2$Cl$_2$ (perhaps only formally in a redox reaction), thus leading to the situation shown in Scheme 2 for step (b).

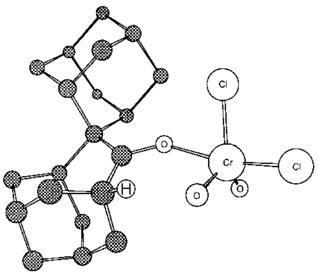

Figure 2. Structure of **2** as optimized by DFT methods (B3LYP, LANL2DZ); d(Cr=O ··· H$_\alpha$) = 2.18 Å.

The final step (c) is of a kind that has been subject to intense discussion in the past:[2, 3] the radical formed adds to a Cr^{VI}=O function to yield an O=Cr^V alkoxide. Exactly this type of reactivity, which is manifested in **3**, has been put forward[2, 3] to explain alcohol formation in alkane oxidations with CrO$_2$Cl$_2$ (vide supra; hydrolysis of **3** provides—as expected—the corresponding α-hydroxy ketone in good yields). Moreover the addition of organic radicals to d^0-M=O bonds had been proposed before, for example: 1) to rationalize the trapping of radicals by CrO$_4^{2-}$ and MnO$_4^-$,[4] 2) to explain the formation of acrolein during the propene oxidation at MoO$_3$/Bi$_2$O$_3$ catalysts, which is assumed to proceed via allyl radicals,[11] and 3) to understand the electron transfer from methyl radicals to d^0 metal ions during methane oxidation on metal oxide surfaces[12] as well as in the gas phase.[13] The identification of the molecular compound **3**, whose isolation and characterization following reaction of BAE with CrO$_2$Cl$_2$ was possible due to special advatageous settings, provides forthright evidence for this fundamental type of reaction on a molecular level.

Experimental Section

3 · CH$_2$Cl$_2$: A solution of BAE (2.00 g, 7.03 mmol)[9] in CH$_2$Cl$_2$ (20 mL) was frozen to −196 °C and CrO$_2$Cl$_2$ (3.25 g, 20.98 mmol) were condensed on top of the frozen block. The mixture was allowed to warm to 0 °C and then stirred at that temperature for 5 h. Avoiding further warming, all volatiles were removed under vacuum, and after washing with n-hexane the brown residue was extracted with CH$_2$Cl$_2$. Cooling of the filtrate yielded analytically pure **3** · CH$_2$Cl$_2$ as brown crystals. Yield: 2.60 g, 70.7 %. IR (KBr): $\tilde{\nu}$ = 1568(s) (ν(C=O)), 988(vs) (ν(Cr=O)) cm^{-1}; ESR (298 K): g = 1.9864, ΔH_{pp} = 20.6 G.

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[7] **3** $\cdot$ CH_2Cl_2: $C_{20}H_{27}Cl_2CrO_3 \cdot CH_2Cl_2$, $M_r = 523.26$, monoclinic, space group $C2/c$, $Z = 8$, $a = 22.574(5)$, $b = 10.534(2)$, $c = 20.629(4)$ Å, $\beta = 117.06(3)$, $V = 4368.5(15)$ Å^3, $4.1 < 2\theta < 52.1°$, ω scan, $T = 200$ K, $\rho_{calcd} = 1.591$ g cm^{-3}, 34592 measured reflections, 4300 independent, and 3534 observed reflections with $I > 2\sigma(I)$, Lp-correction ($\mu = 1.035$ mm^{-1}), 264 refined parameters with $R = 0.032$, residual electron density: max/min: $0.404/-0.309$ e Å^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, the structure was solved by direct methods (SHELXS-97), and refined versus F^2 (SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms. 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-115684. 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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Highly Ordered Columnar Structures from Hexa-*peri*-hexabenzocoronenes—Synthesis, X-ray Diffraction, and Solid-State Heteronuclear Multiple-Quantum NMR Investigations[**]

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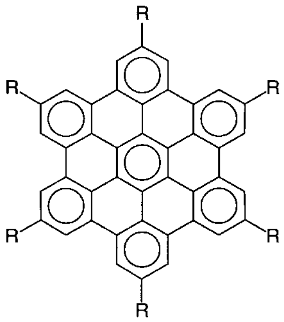
Hans Wolfgang Spiess*

The generation of new functional materials requires both intelligent design and the high-yield synthesis of tailor-made building blocks, as well as methods that enable the highly selective characterization of their organization into supermolecular structures.[1] Interdisciplinary studies involving advanced physical charaterization methods, closely coupled with the synthetic work, is the key to success. Herein, we present an example of such an endeavor through the development of new columnar structures.



1 (R = H)
1a (R = *n*-$C_{12}H_{25}$)

Hexa-*peri*-hexabenzocoronene (HBC, **1**) with long chain alkyl substituents, such as $C_{12}H_{25}$ (HBC-C_{12} **1a**) or $C_{14}H_{29}$, is of considerable interest on account of the unusually large liquid crystalline (LC) phase widths and favorable physical, electronic, and optoelectronic properties that are obtained. An example of such a property is their very high one-dimensional charge carrier mobility.[2] In addition, HBC-C_{12} has the ability to form adsorbate layers on graphite, which have been investigated by scanning tunneling microscopy (STM).[3] These substituted HBCs form columnar liquid crystals,[4] in which the aromatic cores undergo rapid axial rotation on the μs time scale, although the order parameter of the discs, $S = 0.84$, is found to be considerably lower than in other columnar discotics.[5] Since high mobility and low order limit the charge carrier mobility, we set out to synthesize a less mobile mesogen, which at the same time should improve the hexagonal columnar ordering. With this in mind, phenyl rings were inserted between the planar HBC discs and the pendent alkyl chains. In this communication we report the synthesis of hexa(*para*-*n*-dodecylphenyl)-substituted HBC (HBC-PhC_{12},

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