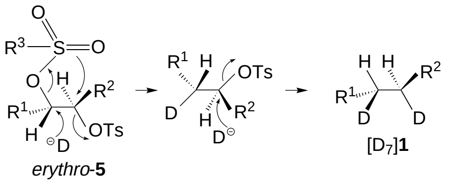

Scheme 2.

tosylate group by the leaving tosyl ester group, thus causing an inversion of configuration at this site. A second inversion at this C atom would then occur by substitution of the remaining tosyl group by a further deuteride ion. The extent of the reduction also occurring through the a priori expected mechanism has not been quantified, but the fact that the proportion of isotopomers of both methyl (*Z*)- and (*E*)-11-tetradecenoate formed from both [D_7]**1** and [D_7]**2** are similar to those formed from the same probes obtained by direct deuteration of the olefins[2] indicates that the unexpected mechanism largely predominated over the expected one. As mentioned above, a similar reaction has been reported by Lin and Shi[8] in the nucleophilic substitution of a 1,2-dimesylate (mesylate = methanesulfonate) with a tosylamine. However, the occurrence of this anchimeric effect is not apparently general. For instance, a cyclic vicinal dimesylate reacts with sodium azide to give the corresponding vicinal diazido derivative arising from single S_N2 displacements at both carbon atoms.[14] Likewise, ditosylates *erythro*- and *threo*-**5** (Scheme 1) react with CsF in polyethyleneglycol to give the corresponding *erythro*- and *threo*-difluorides, respectively.[15]

In summary, we have demonstrated the usefulness of enzymatic reactions as analytical tools to evidence configurational changes not detectable by current analytical techniques. Finally, our results prove that care must be taken when introducing deuterium labeling by reduction of *vic*-ditosylates (and probably other related sulfonate esters) with lithium aluminum deuteride if the configuration of the final products is important.

Received: June 22, 1998 [Z12030IE]
German version: *Angew. Chem.* **1999**, *111*, 121–123

Keywords: deuterations · fatty acids · reaction mechanisms

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Insertion of O_2 into a Chromium–Phenyl Bond: Mechanism of Formation of the Paramagnetic d^2 Oxo Complex [$Tp^{tBu,Me}Cr^{IV}(O)OPh$]**

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The oxidative functionalization of organic molecules utilizing dioxygen as a reagent remains one of the major challenges for research in catalysis.[1] The ready availability of O_2 and the absence of environmentally harmful by-products are among the attractive features of such processes. Fundamental studies of the role of transition metals in catalytic oxidation must naturally include investigations of the reaction pathways of organometallic molecules with O_2. In this context, the insertion of O_2 into metal–carbon bonds is a reaction of central importance. Despite its significance, only relatively few mechanistic studies of this transformation are available.[2] Herein we report an investigation of the reaction of O_2 with a tris(pyrazolyl)borate chromium phenyl complex, which ultimately yields a phenoxide.

Exposure of a cold ($-45\,^\circ C$) solution in pentane of [$Tp^{tBu,Me}CrPh$][3] (**1**; $Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) to an excess of O_2 led to a rapid color change from blue to red. Upon warming to ambient temperature the color of the solution changed again, from red to brown, and workup of the reaction mixture provided the complex [$Tp^{tBu,Me}Cr(O)OPh$] (**2**), which could be isolated in moderate yield (48%; see Scheme 1). The molecular structure of **2** has been determined by X-ray diffraction,[4] and the result is shown in Figure 1. Despite the steric hindrance of the $Tp^{tBu,Me}$ ligand, which has earned it the title "tetrahedral enforcer",[5] **2** exhibits a five-coordinate chromium atom in a trigonal-bipyramidal configuration. The apparent product of the incorporation of one equivalent of O_2, **2** exhibits an equatorial oxo ligand and an axial phenoxide moiety, which formally results from the insertion of an oxygen atom into the erstwhile chromium–carbon bond. The oxidation state of chromium in the new complex is +IV (d^2); hence, **2** is chemically related to oxo complexes of the type [(porphyrinato)$Cr^{IV}(O)$].[6] However, in contrast to the latter and as indicated by its isotropically shifted and broadened ^1H NMR resonances, **2** is paramagnetic, and its effective magnetic moment in the solid state ($\mu_{eff}(293\,K) = 2.6(1)\,\mu_B$) is consistent with two unpaired electrons. Paramagnetism of a d^2 mono-oxo complex is rather unusual.[7] We suggest that both frontier orbitals (i.e., d_{xz} and d_{yz}; the z axis is along N(3)-Cr-O(2)) are

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[**] This research was supported by grants from the U. S. National Science Foundation and the U. S. Department of Energy. We thank Applied Systems Inc. for the donation of a ReactIR 1000 instrument.

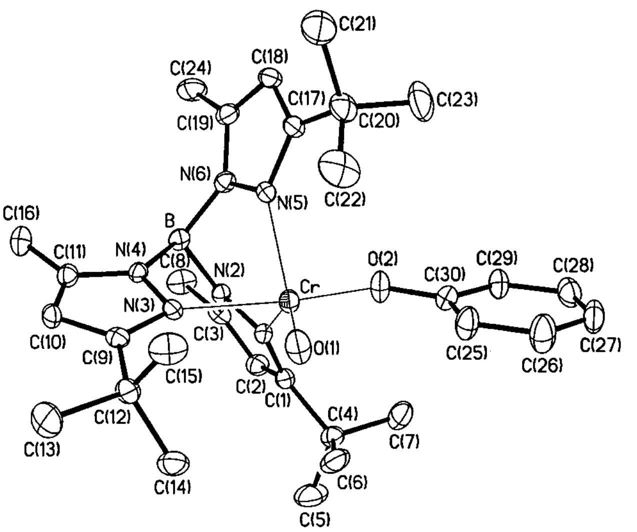


Figure 1. The molecular structure of trigonal-bipyramidal **2**. Selected interatomic distances [Å] and angles [°]: Cr–O(1) 1.576(3), Cr–O(2) 1.844(3), Cr–N(1) 2.097(4), Cr–N(3) 2.191(4), Cr–N(5) 2.099(4); Cr-O(2)-C(30) 136.7(3), O(1)-Cr-O(2) 103.8(2), O(1)-Cr-N(1) 130.2(2), O(1)-Cr-N(3) 87.9(2), O(1)-Cr-N(5) 128.7(2), O(2)-Cr-N(1) 89.7(2), O(2)-Cr-N(3) 168.2(2), O(2)-Cr-N(5) 90.7(2), N(1)-Cr-N(3) 81.46(14), N(1)-Cr-N(5) 98.1(2), N(3)-Cr-N(5) 82.95(14).

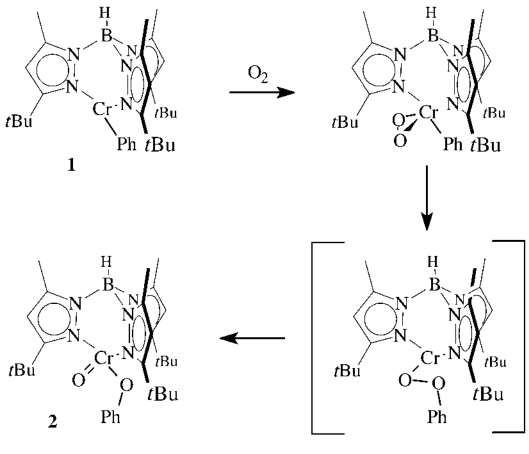
destabilized by competitive π donation from the oxo and the phenoxo ligands, respectively; apparently the resulting split in their degeneracy does not suffice to enforce spin pairing.

The spectroscopic characterization of **2** is in accordance with its solid-state structure. Specifically, its IR spectrum (KBr pellet) exhibited a strong band at 922 cm^{-1}, assigned as $\nu_{Cr=O}$, which was shifted to 884 cm^{-1} upon substitution by ^{18}O. The ^1H NMR spectrum ([D_8]toluene, room temperature) showed three broad resonances ($\delta = 17.5$ (9H), 9.4 (27H), and 1.5 (3H)) due to the protons of the $Tp^{tBu,Me}$ ligand, indicating fluxionality of the five-coordinate molecule. This rearrangement can be slowed on the time scale of the NMR experiment by cooling the sample below 180 K. For the identification of the less intense resonances of the phenoxide ligand, deuterium labeling proved indispensable.[8] The ^2H NMR spectrum of [$Tp^{tBu,Me}Cr(O)OC_6D_5$] ([D_5]-**2**) revealed three reasonably sharp resonances at $\delta = 17.4$ (2D), -31.7 (1D), and -33.6 (2D). In the ^1H NMR spectrum of **2** the first of these was obscured by a Tp ligand resonance, and the latter two were not resolved due to the greater line width of ^1H resonances of paramagnets. All resonances exhibited the expected temperature dependence (i.e., $\delta_{iso} \propto 1/T$).

Important questions concerning the formation of **2** include the nature of the intermediate observed at low temperature and the detailed mechanism of the oxygen insertion. A dioxygen adduct ([$Tp^{tBu,Me}Cr(O_2)Ph$]), a phenyl peroxide ([$Tp^{tBu,Me}CrOOPh$]), or a dioxo phenyl complex resulting from oxidative addition of O_2 to Cr^{II} ([$Tp^{tBu,Me}Cr(O)_2Ph$]) are among the possible candidates for the intermediate. We sought to address this question by in situ IR spectroscopy. Exposure of a stirred, cold (-78 to $-50\,^{\circ}C$) solution in toluene of **1** (ca. 0.5 M) to O_2 led to a gradual replacement of the characteristic signals of the starting material with a new set of bands. The absence of any strong bands attributable to $\nu_{Cr=O}$ ($\approx 920\ cm^{-1}$) or ν_{C-O} ($\approx 1280\ cm^{-1}$) was notable. Repetition of the experiment with $^{18}O_2$ afforded a spectrum that was indistinguishable except for the position of one resonance, which had been shifted from 1027 cm^{-1} (^{16}O) to 969 cm^{-1} (^{18}O). Based on these observations we propose that the first observable intermediate of the reaction of **1** with O_2 is a Cr^{III} superoxo complex, that is, [$Tp^{tBu,Me}Cr(O_2)Ph$].[9] The well-known preference of Cr^{III} for octahedral coordination and the similarity in the vibrational spectra to that of [$Tp^{tBu,Me}Co(O_2)$] suggests that the superoxo ligand may well be coordinated in the side-on fashion (η^2-O_2),[10] although the more common end-on coordination (η^1-O_2) is also possible. Upon warming of the solution of [$Tp^{tBu,Me}Cr(O_2)Ph$] to room temperature, its IR spectrum was smoothly transformed into that of **2**, ruling out the intervention of another spectroscopically observable intermediate.

The reaction of metal–alkyl complexes with O_2 may proceed by a radical chain process, involving an S_H2 displacement of $R^{\bullet}$ by $ROO^{\bullet}$, rather than an intramolecular insertion of O_2 into the M–R bond.[2a–d] To distinguish between these two pathways, we have performed a crossover experiment. When an equimolar solution of [$Tp^{tBu,Me}CrC_6D_5$] and [$Tp^{tBu}CrC_6H_5$] was allowed to react with O_2, ^2H NMR analysis of the product mixture showed the presence of [$Tp^{tBu,Me}Cr(O)OC_6D_5$] as the only major deuteriated product. Specifically, only a very small amount of the crossover product—that is, [$Tp^{tBu}Cr(O)OC_6D_5$] (which was independently prepared and characterized spectroscopically)—was detected; the latter is thought to result from a slow scrambling process occurring in the starting mixture. This observation indicates that the insertion of O_2, starting from the adduct [$Tp^{tBu,Me}Cr(O_2)Ph$], proceeds in an intramolecular fashion.

Based on the observations summarized above we propose a mechanism for the reaction of **2** with O_2 (Scheme 1). The postulated phenylperoxo intermediate resulting from insertion of O_2 into the Cr–Ph bond was not observed directly and is inferred. However, several factors militate against a pathway involving its possible alternative, that is, [$Tp^{tBu,Me}Cr(O)_2Ph$]. First, the coordination of three independent ligands to a transition metal in addition to the $Tp^{tBu,Me}$ ligand is unprecedented, due to the steric demand of the



Scheme 1. Proposed mechanism for the formation of **2** from **1** and O_2.

latter.[11] Furthermore, its stable cyclopentadienyl analogue [Cp*Cr(O)$_2$Me] does not rearrange to [Cp*Cr(O)OMe].[12] In general, the migratory insertion of oxo ligands into metal–carbon single bonds appears to be an unfavorable process.[13] It is unlikely to be kinetically competent to explain the ready transformation of **1** into **2**.

The isolation of **2** extends the scarce tris(pyrazolyl)borate chemistry of chromium to its relatively rare +IV oxidation state. It also demonstrates that there exist facile intramolecular pathways for the oxygenation of metal–carbon σ bonds by migratory insertion of O_2. Such transformations may serve as individual steps in metal-catalyzed oxidations of organic molecules by air.

Experimental Section

All experiments were carried out under exclusion of air and moisture with inert atmosphere glove box, Schlenk, or high vacuum line techniques.

2: A solution of **1** (0.50 g, 0.91 mmol) in pentane (50 mL) was charged into a glass ampoule equipped with a Teflon stopcock. After the solution was cooled to $-45\,^{\circ}C$, the ampoule was evacuated and then filled with dry O_2. The color of the solution changed immediately from blue to red. After the solution was stirred for 0.5 h, it was allowed to warm to room temperature, whereupon it turned brown. The solvent was evaporated, and the solid residue was recrystallized from Et_2O at $-30\,^{\circ}C$ to yield light brown crystals of **2** (0.254 g, 48 %). M.p. 98 °C; ^1H NMR (250 MHz, [D_6]benzene, 25 °C): $\delta = 17.5$ (br, 9H), 9.4 (br, 27H), 1.5 (br, 3H), -35.4 (br, 3H); IR (KBr): $\tilde{\nu} =$ 3053, 2961, 2545, 1587, 1543, 1478, 1424, 1350, 1282, 1261, 1194, 1070, 1024, 922, 866, 292, 659 cm^{-1}; UV/Vis (Et_2O): λ_{max} (ε) = 415 nm (1730); μ_{eff} (25 °C) = 2.6(1) μB; elemental analysis for $C_{30}H_{45}BCrN_6O_2$: calcd (found): C 61.64 (61.38), H 7.76 (7.02).

The in-situ IR spectroscopic monitoring of the reaction of **1** with O_2 was carried out with an Applied Systems Inc. ReactIR 1000 instrument, equipped with a DiComp probe. The probe was inserted directly into a cooled ($-78\,^{\circ}C$ initially) solution of **1** in toluene (0.5 M). Spectra were acquired at 4-cm^{-1} resolution, and a background spectrum of toluene was subtracted.

Received: June 23, 1998 [Z12034IE]
German version: *Angew. Chem.* **1999**, *111*, 126–128

Keywords: chromium · insertions · O–O activation · oxygenations · tripodal ligands

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A Novel Highly Charged (+12) Anion Receptor That Encapsulates Simultaneously NO_3^- and PF_6^- Ions**

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Recently we described a molecular triangle, [{(en)Pt(bpz)}$_3$](NO$_3$)$_6$, consisting of three (en)Pt^{II} entities (en = ethylenediamine) and three 2,2′-bipyrazine (bpz) ligands that bridge metals through N(4) and N(4′).[1] In this compound the pyrazine rings adopt a transoid arrangement and are markedly twisted. We have now found that addition of chelating metal entities, for example (en)Pd^{II}, to this compound causes rotation of a pyrazine ring about the central C(2)–C(2′) bond and coordination of the heterometal atom at the N(1) and N(1′) positions. The hexanuclear cation formed in the presence of (en)Pd^{II} has a charge of +12 and exhibits a high affinity for anions. The X-ray crystal structure of [{(en)Pt(bpz)Pd(en)}$_3$](NO$_3$)$_4$(PF$_6$)$_8$ (**1**) confirms the simultaneous encapsulation of NO_3^- and PF_6^- ions in the cavity of

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[**] This work was supported by the Fonds der Chemischen Industrie. We thank R. K. O. Sigel for the introduction in the association constant determination.