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Investigation of Chromium Complexes with a Series of Tripodal Ligands

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Abstract. A series of chromium(II) complexes containing the tripodal ligands tmpa, Me_2uns-penp, Me_4apme and Me_6tren were prepared and investigated with regard to their reactivity towards dioxygen. It was possible to structurally characterize the complexes $[Cr(Me_2\text{uns-penp})Cl]_2(BPh_4)_2$, $[Cr(Me_6\text{tren})Cl]Cl$, $[Cr(Me_4\text{apme})Cl]BPh_4$ and $[Cr(Me_4\text{ampe})Cl_3]$. The complexes show reactions with dioxygen, but it was not possible to characterize intermediates of these reactions. The oxidation behavior of the complexes towards organic substrates like toluene was investigated and oxidation of toluene to benzaldehyde was observed.

Introduction

Oxidation reactions play an important role in biochemistry, industrial processes, and organic syntheses.[1] Therefore, there is high interest in the direct oxidation of organic substrates using a metal catalyst and air as the oxidant.

The activation of dioxygen leads to different "dioxygen adduct" transition metal complexes such as, for example, superoxido, peroxido or oxido species. The formation of "dioxygen adduct" complexes can cause the transfer of oxygen to a substrate. In that regard *Würtele* et al. as well as *Karlin* and co-workers recently demonstrated that a copper peroxido complex could be used to oxidize toluene to benzaldehyde and benzyl alcohol.[2] The copper peroxido complexes used in these investigations were based on the tripodal ligands shown in Figure 1. However, oxidations in organic syntheses are still often performed using chromium(VI) compounds such as $K_2Cr_2O_7$. These compounds are problematic with regard to selective oxidation reactions and their toxicity.[3] With this background it seemed interesting to investigate the possibility to perform selective oxidation reactions with low valent chromium complexes and dioxygen using the tripodal ligands shown in Figure 1.

Especially tris(2-pyridylmethyl)amine (tmpa, Figure 1) has turned out to be a versatile ligand in bioinorganic chemistry to model the reactivity of different metal enzymes based on iron, copper, manganese or zinc in the active centre as well as in other applications.[4] Most importantly, tmpa was used in copper chemistry where *Karlin* and co-workers succeeded in structurally characterizing a dinuclear copper peroxido complex for the first time. They were able to model the reversible uptake of dioxygen of copper enzymes.[5]

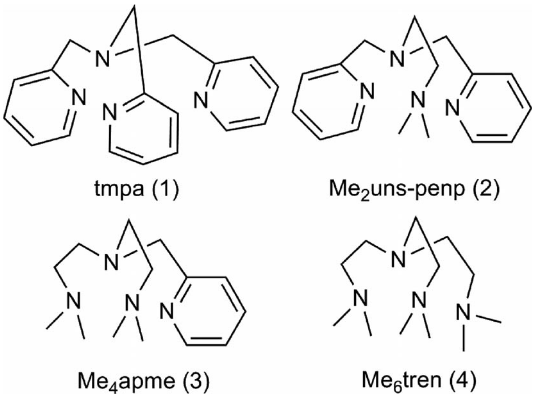

Figure 1. Tripodal ligands investigated in this work.

Systematic variation of the ligand tmpa was performed in the past in an effort to gain better understanding of the reactivity of copper(I) complexes towards dioxygen and the potential of the formed intermediates to oxidize organic substrates.[6] In the ligands in Figure 1 the pyridine N-donor atoms of tmpa were systematically substituted with aliphatic amine donor atoms leading from tmpa (**1**) to (2-dimethyl-aminoethyl)bis(2-pyridylmethyl)amine (Me_2uns-penp (**2**)), bis(2-dimethylaminoethyl)(2-pyridylmethyl)amine (Me_4apme (**3**)) and tris(2-dimethyl-aminoethyl)amine (Me_6tren (**4**)). Copper(I) complexes with all of these four ligands react with dioxygen to form a mononuclear end-on superoxido copper complex that further reacts to a dinuclear copper peroxido complex according to the mechanism shown in Figure 2.[7]

The peroxido complex $[(Me_6\text{tren})CuO_2(Me_6\text{tren})]^{2+}$ was structurally characterized.[2a] As described above it could be demonstrated that these complexes can be used to catalytically oxidize toluene to benzaldehyde.[2a] However, one of the problems to investigate these compounds in solution is the necessity to perform all these studies at low temperatures. Therefore,

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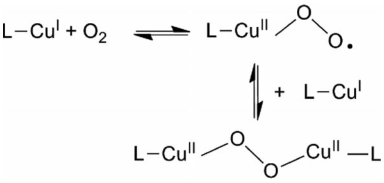


Figure 2. Mechanism for the reaction of copper(I) complexes (L = tripodal ligand) with dioxygen (Charges are omitted for clarity).

low temperature stopped-flow measurements were performed. Unfortunately, even at –80 °C detection, many times the reaction intermediates could not be spectroscopically identified fast enough.[6b,7]

Due to the fact that stable chromium peroxido complexes are well known, e.g. $[Cr(dien)(O_2)_2]{\cdot}H_2O$ (dien = diethylenetriamine),[8] we assumed that we might overcome some of these problems using chromium complexes with the tripodal ligands shown in Figure 1. Further support for this assumption came from *Nam* and co-workers who recently succeeded to structurally characterize a superoxido chromium(III) complex using TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) as a ligand.[9] Furthermore, they obtained the according chromium(IV) or chromium(V) oxido complexes.[10] Using the smaller macrocycle cyclen as a ligand a side-on peroxido chromium(IV) complex was prepared and structurally characterized by the same group.[11] Reactivity studies demonstrated the interesting potential of these complexes.

Results and Discussion

Chromium(II) complexes with the ligand tmpa were previously reported by *Robertson* et al.[12] They structurally characterized complexes $[Cr(tmpa)Cl_2]$ (**1a**) and $[Cr(tmpa)Cl]_2(BPh_4)_2$ (**1b**). We were able to reproduce their syntheses of both compounds. Furthermore, they described that from the reaction of **1b** in acetonitrile (with traces of water or air in the solvent) the formation of a μ-oxido chromium(III) complex, $\{[Cr(tmpa)Cl]_2(\mu\text{-}O)\}(BPh_4)_2$, was observed as an impurity. This compound was structurally characterized as well, however, no spectroscopic data were reported. We thus reacted **1b** with dioxygen in acetonitrile to enforce this reaction and observed the spectral changes in the UV/Vis spectrum as shown in Figure 3.

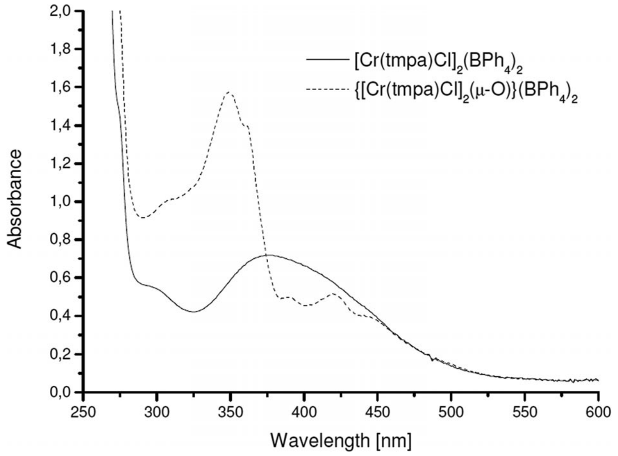


Figure 3. UV/Vis spectrum of **1b** (solid line) and product complex (dashed line) after passing dioxygen through the solution (CH_3CN, 25.0 °C, complex concentration = 0.8 mmol·L^{-1}).

The spectrum of **1b** shows two absorption maxima at 306 nm and at 376 nm as described in literature.[12] After reaction with dioxygen the spectrum changed and new absorption bands at 349 nm with a shoulder at 363 nm as well as at 393, 420 and 446 nm were observed. The infrared spectrum showed a Cr–O–Cr stretching vibration at 844 cm^{-1}. The spectroscopic data compare well with other related μ-oxido chromium complexes described previously.[13]

Avoiding chloride as an additional ligand we performed the reaction of $Cr(OTf)_2{\cdot}4H_2O$ with tmpa in acetonitrile. From this reaction we obtained crystals suitable for crystallographic analysis that showed that a bis(μ-hydroxido) chromium(III) complex was obtained. The molecular structure of the cation of $[Cr(tmpa)OH]_2(OTf)_4$ (**1c**) is reported in the Supporting Information. The same reaction has been previously observed by *Gafford* et al. when $[Cr(tmpa)](ClO_4)_2$ reacted with dioxygen in ethanol.[13a] This bis(μ-hydroxido) chromium(III) dimer has also been reported by *Hodgson* et al.[14] and *Gafford* et al.[15] with perchlorate or bromide as anions. All these bis(μ-hydroxido) complexes showed a similar UV/Vis spectrum with absorption maxima at 386 nm and 540 nm.

Using the synthetic protocol of *Robertson* et al. for the tmpa complexes we prepared the according complexes with the ligands Me_2uns-penp, Me_4apme and Me_6tren in a similar way without any problems. Crystals suitable for structural analysis could be obtained at approx. –40 °C for the complexes described below. The crystallographic data are summarized in Table 1.

The crystallographic data of $[Cr(Me_2\text{uns-penp})Cl_2]$ (**2a**) are reported in the Supporting Information. Its molecular structure is very similar to **1a**. In both complexes the two chloride anions are coordinated to the chromium ion. The molecular structure of the cation of $[Cr(Me_2\text{uns-penp})Cl]_2(BPh_4)_2$ (**2b**) is presented in Figure 4. Selected bond lengths and angles are summarized in Table 2. **2b** crystallized as a dimer. One unit of this complex has a distorted square pyramidal coordination (τ = 0.31).[16] Two of these units are connected through two chloride bridges. The bond length Cr–Cl(1)* is longer than the bond length between chromium and the coordinated chloride. Cr(1)–Cl(1)* = 3.278 Å vs. Cr(1)–Cl(1) = 2.3358(9) Å. This observation is in accordance to the observations for the tmpa complex as described previously by *Robertson* et al.[12]

Crystals of **3a** suitable for crystal structure analysis could be obtained, but refinement was not possible. However, complex $[Cr(Me_4\text{apme})Cl]BPh_4$ (**3b**) could be crystallized. Figure 5 shows the molecular structure of the cation of **3b** (selected bond lengths and angles are summarized in Table 2). In contrast to **1b** and **2b** it crystallizes as a monomer. The arrangement is best described as an intermediate between a square pyramidal and trigonal bipyramidal coordination (τ = 0.57).[16]

Furthermore, a chromium(III) complex with the ligand Me_4apme, $[Cr(Me_4\text{apme})Cl_3]$ (**3d**), could be crystallized as a

Table 1. Crystallographic data.

	2b	**3b**	**4a**	**3d**
Formula	$C_{40}H_{42}BClCrN_4$	$C_{38}H_{46}BClCrN_4$	$C_{12}H_{30}Cl_2CrN_4$	$C_{14}H_{26}Cl_3CrN_4$
Formula weight	677.04 $g\cdot mol^{-1}$	657.05 $g\cdot mol^{-1}$	353.30 $g\cdot mol^{-1}$	408.74 $g\cdot mol^{-1}$
Temperature	193(2) K	193(2) K	193(2) K	190(2) K
Wavelength	0.71073 A	0.71073 A	0.71073 A	0.71073 A
Crystal system	monoclinic	orthorhombic	cubic	triclinic
Space group	$P2_1/n$	$Pbca$	$P2_13$	$P\bar{1}$
Unit cell dimensions	a = 14.9600(3) Å b = 16.2770(3) Å c = 15.9060(3) Å α = 90° β = 117.35(3)° γ = 90°	a = 16.2700(3) Å b = 16.6890(3) Å c = 25.4950(5) Å α = 90° β = 90° γ = 90°	a = 11.9655(14) Å b = 11.9655(14) Å c = 11.9655(14) Å α = 90° β = 90° γ = 90°	a = 7.1750(14) Å b = 8.7870(18) Å c = 16.2250(3) Å α = 97.88(3)° β = 93.92(3)° γ = 112.27(3)°
Cell volume	3440.2(12) $Å^3$	6923(2) $Å^3$	1713.1(3) $Å^3$	929.6(3) $Å^3$
Z/Calculated density	4, 1.307 $Mg\cdot m^{-3}$	8, 1.261 $Mg\cdot m^{-3}$	4, 1.370 $Mg\cdot m^{-3}$	2, 1.460 $Mg\cdot m^{-3}$
Absorption coefficient	0.445 mm^{-1}	0.440 mm^{-1}	0.974 mm^{-1}	1.048 mm^{-1}
$F(000)$	1424	2784	752	426
θ range	2.83 to 28.12°	1.92 to 24.22°	3.81 to 28.07°	2.54 to 27.46°
Limiting indices	$-19 \le h \le 19$, $-20 \le k \le 20$, $-20 \le l \le 21$	$-18 \le h \le 18$, $-19 \le k \le 19$, $-29 \le l \le 29$	$-14 \le h \le 15$, $-15 \le k \le 15$, $-14 \le l \le 15$	$-9 \le h \le 9$, $-11 \le k \le 11$, $-21 \le l \le 20$
Reflections collected / unique	30871 / 8273 [R(int) = 0.0924]	40311 / 5555 [R(int) = 0.1426]	15301 / 1404 [R(int) = 0.1200]	15992 / 4250 [R(int) = 0.0973]
Completeness to θ	98.4 %	99.7 %	99.6 %	99.7 %
Absorption correction	none	none	none	none
Refinement method	Full-matrix least-squares on F^2			
Data / restraints / parameters	8273 / 0 / 426	5555 / 0 / 410	1404 / 0 / 76	4250 / 0 / 303
Goodness-of-fit on F^2	0.839	0.827	0.977	1.029
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0471, wR_2 = 0.1027	R_1 = 0.0510, wR_2 = 0.1143	R_1 = 0.0427, wR_2 = 0.0896	R_1 = 0.0523, wR_2 = 0.1297
R indices (all data)	R_1 = 0.1002, wR_2 = 0.1153	R_1 = 0.1140, wR_2 = 0.1299	R_1 = 0.0647, wR_2 = 0.0974	R_1 = 0.0777, wR_2 = 0.1425
Largest diff. peak and hole	0.515 and -0.385 $e\cdot Å^{-3}$	0.596 and -0.269 $e\cdot Å^{-3}$	0.407 and -0.411 $e\cdot Å^{-3}$	1.015 and -0.809 $e\cdot Å^{-3}$

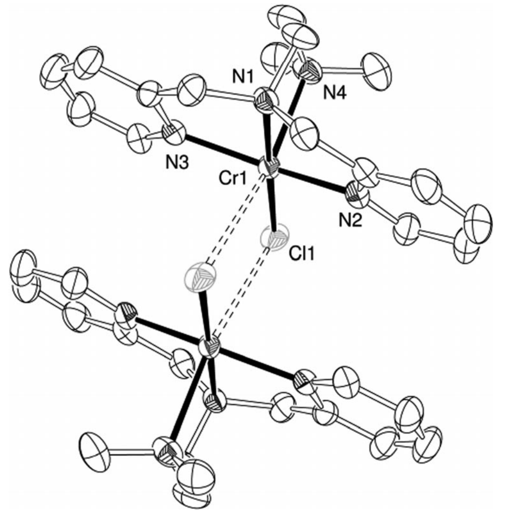


Figure 4. Molecular dimer structure of the cation of **2b** shown as an ORTEP plot with thermal ellipsoids set at 50 % probability.

Table 2. Selected bond length /Å and bond angles /°.

	2b	**3b**	**4a**	**3d**
Cl(1)–Cr(1)	2.3358(9)	2.3180(13)	2.3346(18)	2.3406(11)
Cl(1)*–Cr(1)	3.278	–	–	–
Cl(2)–Cr(1)	–	–	–	2.3150(13)
Cl(3)–Cr(1)	–	–	–	2.3161(11)
Cr(1)–N(2)	2.076(2)	2.107(4)	2.219(3)	2.153(2)
Cr(1)–N(3)	2.090(2)	2.142(4)	2.219(3)	2.168(3)
Cr(1)–N(1)	2.110(2)	2.110(4)	2.114(5)	2.096(3)
Cr(1)–N(4)	2.402(2)	2.337(4)	2.219(3)	–
N(2)–Cr(1)–N(3)	158.71(9)	83.83(17)	118.46(3)	83.88(10)
N(2)–Cr(1)–N(1)	79.83(9)	79.70(14)	82.82(8)	78.56(10)
N(3)–Cr(1)–N(1)	81.41(9)	143.15(15)	82.82(8)	92.27(11)
N(2)–Cr(1)–N(4)	97.94(9)	80.28(15)	118.46(3)	–
N(3)–Cr(1)–N(4)	88.86(9)	111.30(15)	118.46(3)	–
N(1)–Cr(1)–N(4)	80.71(8)	98.13(15)	82.82(8)	–
N(2)–Cr(1)–Cl(1)	98.00(7)	177.52(12)	97.18(8)	91.05(8)
N(3)–Cr(1)–Cl(1)	100.46(7)	98.52(12)	97.18(7)	174.92(7)
N(1)–Cr(1)–Cl(1)	177.42(7)	97.90(11)	180.00(7)	87.10(8)
N(4)–Cr(1)–Cl(1)	101.05(6)	99.54(11)	97.18(8)	–
Cl(1)–Cr(1)–Cl(1)*	95.18	–	–	–

by-product of the synthesis of complex **3a**. Upon crystallization we obtained a mixture of **3a** and **3d** that allowed picking of crystals of both compounds suitable for crystal structure analysis. Obviously, some part of the chromium(II) complex has been oxidized during the synthesis leading to this mixture. The molecular structure of [Cr(Me_4ampe)Cl_3] (**3d**) is shown in Figure 6 (selected bond lengths and angles can be found in Table 2). This complex is sixfold coordinated with three chloride ligands and three N-donor atoms of the ligand Me_4apme. One aliphatic arm of the ligand is not coordinated, because it has been replaced by a chloride ion. This behavior is well known from related copper chemistry.[17]

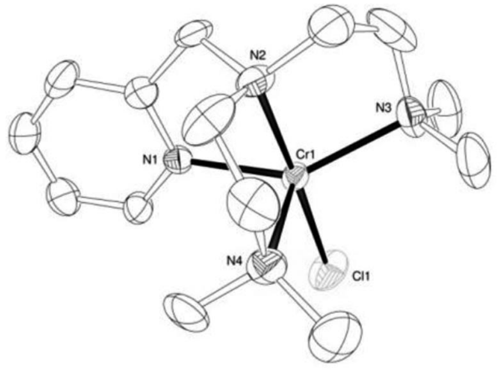


Figure 5. Molecular structure of the cation of **3b** shown as an ORTEP plot with thermal ellipsoids set at 50 % probability.

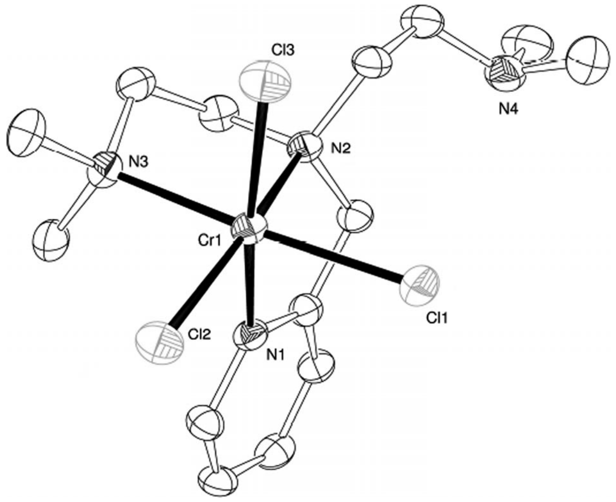


Figure 6. Molecular structure of **3d** shown as an ORTEP plot with thermal ellipsoids set at 50 % probability.

Furthermore, complexes with Me_6tren as ligand were structurally characterized. Figure 7 shows the molecular structure of the cation of [Cr(Me_6tren)Cl]Cl (**4a**). In contrast to the complexes of **1a** and **2a** complex **4a** is coordinated only by one chloride ligand. The complex is fivefold coordinated and has trigonal bipyramidal coordination (τ = 1).[16] Therefore complex **4a** is quite similar to [Cr(Me_6tren)Cl]BPh_4 (**4b**). The molecular structure and crystallographic data of **4b** are reported in the Supporting Information. **4b** again crystallizes as a monomeric unit that has perfect trigonal bipyramidal coordination (τ = 1).[16]

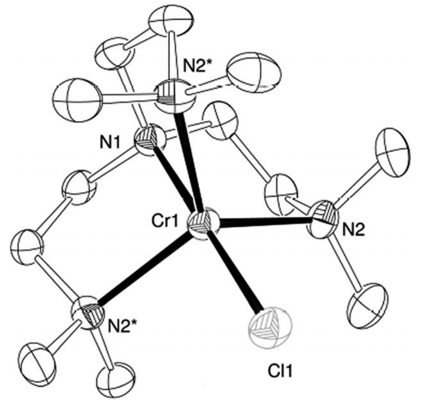
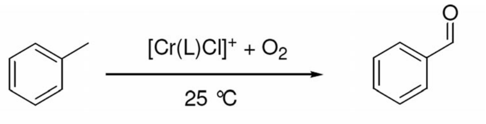


Figure 7. Molecular structure of the cation of **4a** shown as an ORTEP plot with thermal ellipsoids set at 50 % probability.

Oxidation of Toluene

All synthesized chromium complexes were tested for their potential as catalysts for the oxidation of toluene in comparison with the analogous reaction of the according copper complexes reported previously.[2a] For this investigation the complexes were dissolved in a minimum of a mixture of acetone and toluene and then dioxygen was passed through the solution. The resulting product solutions were analyzed by GC–MS spectrometry. **1a**, **2a**, **3a** and **4a** showed no oxidation potential towards toluene. GC–MS measurements showed no oxidation products of toluene. In contrast, complexes of the type [Cr(L)Cl]BPh_4 demonstrated oxidation potential towards toluene. GC–MS measurements showed that similar to the copper complexes benzaldehyde was formed with a maximum yield for complex **3b** of 25 %. Thus the chromium complexes unfortunately were not better than analogous copper compounds: maximum yield of benzaldehyde with copper complexes was approx. 40 % with L = tmpa.[2] The yields of all chromium complexes are summarized in Figure 8. Due to the quite low yields no further detailed studies were performed on these oxidation reactions.



Complex	Yield (in %)
1b (L = tmpa)	8
2b (L = Me_2uns-penp)	5
3b (L = Me_4ampe)	25
4b (L = Me_6tren)	0

Figure 8. Oxidation of toluene and yield of benzaldehyde in %.

The low yields of benzaldehyde are a consequence of several side reactions that cause formation of e.g. phenylbenzene or 4-phenyl-3-buten-2-one (reaction of benzaldehyde with acetone) in combination with simple oxidation reactions of the chromium(II) complex to a chromium(III) compound.

Whereas it is principally not correct to assume that solid-state structures are retained in solution, one could at least speculate if this is the case for the chromium complexes discussed above. This would give a possible explanation for the different yields of benzaldehyde obtained by oxidation with the four complexes discussed in this study. The nearly perfect trigonal bipyramidal coordination of **4b** seems to suppress reactivity towards a substrate whereas **3b** with an arrangement between square pyramidal and trigonal bipyramidal supports the oxidation reaction of toluene to benzaldehyde. With complexes **1b** and **2b** lower yields were most likely observed due to equilibria of dimers and monomers. Two different mechanistic pathways were suggested by *Lucas* et al. for the oxidation of toluene by copper complexes.[2b] However, these proposed mechanisms so far are not based on solid kinetic studies and might be different for the chromium complexes described in here anyway.

Low Temperature Stopped-Flow Spectroscopy

In regard to the finding that some toluene oxidation was observed with complex **3b**, its reaction with dioxygen was furthermore investigated by low temperature stopped-flow measurements. When **3b** (the spectrum is presented as bold line in Figure 9b) reacted with dioxygen, a new complex rapidly formed (thin line in Figure 9b).

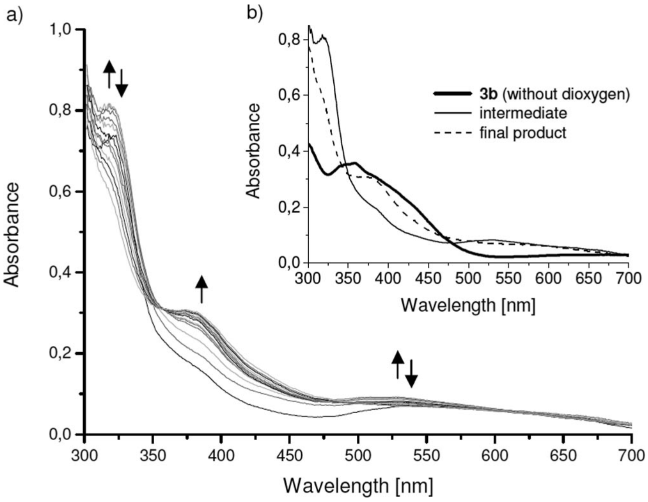


Figure 9. a) Time resolved spectra for the reaction of a 0.5 mmol·L^{-1} solution of **3b** in acetonitrile with dioxygen [0.01 mol·L^{-1}] at –40.0 °C (overall reaction time = 450 s, Δ = 1.5 ms). b) UV/Vis spectrum of **3b** (0.5 mmol·L^{-1} in acetonitrile) and selected single spectra from the stopped-flow experiment.

The spectral features of this new compound (320, 381, 528 and 631 nm) are similar to the reported data for the end-on superoxido chromium(III) complex by *Nam* and co-workers.[9] Unfortunately it was not possible to further characterize this intermediate because in a slower consecutive reaction a different complex formed (dashed line in Figure 9b, absorbance maxima at 319 (shoulder), 378 and 574 nm). So far, the final product of this reaction is unknown. Efforts to isolate and characterize this product complex failed. Furthermore, a detailed kinetic analysis was not possible due to a more complex reaction behavior (parallel reactions – no isosbestic points were observed). In regard to these problems together with low yields on the oxidation of toluene this reaction further was not investigated.

Conclusions

It was demonstrated that chromium(II) complexes with tripodal ligands in principle can be used to oxidize organic substrates with dioxygen as an oxidant. Furthermore, it was shown that this reactivity strongly depends on the tripodal ligand used. Unfortunately, our hope that using chromium complexes as an alternative to copper or iron complexes would simplify our understanding of these reaction mechanisms turned out to be too naive. Similar to related copper chemistry, the reaction behavior of chromium complexes with dioxygen is quite complicated to analyze. Furthermore, we were not able to structurally characterize some of the postulated reactive intermediate chromium “dioxygen adduct” complexes so far. However, the reactivity of the chromium(II) complexes in principle is promising. Optimizations of these reactions using different “better” ligands might lead to an alternative way for oxidation reactions in organic chemistry.

Experimental Section

Materials

Reagents and solvents used were commercially available. Chromium(II) triflate tetrahydrate was prepared according to literature.[18] Furthermore, all tripodal ligands were synthesized according to published procedures.[19]

Equipment

UV/Vis absorption spectra were recorded using an Agilent 8453-spectrometer. The measurements were performed using quartz cuvettes. GC-MS data were obtained using a Quadrupol-MS HP MSD 5971 (EI) with a J&W quartz glass GC column (30 m × 0.25 mm, 0.25 µm DB-5 MS). Stopped-flow experiments at ambient pressures were performed using a commercially available Hi Tech Limited SF-61SX2 (Salisbury, UK) instrument. IR measurements were performed using a JASCO FT/IR-4100 spectrometer. Elemental analyses were obtained using a vario EL III element analyzer from Elementar.

Synthesis of Complexes with the Ligands L = tmpa, Me$_2$uns-penp, Me$_4$apme and Me$_6$tren

The synthesis of these complexes is based on the preparation of the complex [Cr(tmpa)Cl$_2$] (**1a**) and [Cr(tmpa)Cl]$_2$(BPh$_4$)$_2$ (**1b**) described in literature.[12] Complex [Cr(tmpa)OH]$_2$(OTf)$_4$ (**1c**) was also synthesized according to literature.[13a]

[Cr(Me$_2$uns-penp)Cl$_2$] (2a): Anhydrous CrCl$_2$ (0.05 g, 0.37 mmol) and Me$_2$uns-penp (2-dimethyl-aminoethyl)bis(2-pyridylmethyl)-amine) (0.10 g, 0.37 mmol) were stirred in tetrahydrofuran under inert atmosphere. The solution was stirred and a brown precipitate occurred. The solid was collected, dissolved in a minimum of acetonitrile and filtered. Brown crystals could be obtained by ether diffusion at –40 °C. Yield: 0.08 g (55 %). Anal.: $C_{16}H_{22}N_4Cl_2Cr$ (393.27); C 48.46 (calcd. 48.86); H 5.65 (5.64); N 14.73 (14.25) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 257 nm (3.7), 346 nm (3.1), **IR** (KBr): *ν* = 3020, 2985, 2927, 1661, 1604, 1472, 1437, 1288, 1156, 1028, 818, 765, 650 cm^{-1}.

[Cr(Me$_2$uns-penp)Cl]$_2$(BPh$_4$)$_2$ (2b): Anhydrous CrCl$_2$ (0.05 g, 0.37 mmol) and NaBPh$_4$ (0.13 g, 0.37 mmol) were stirred with Me$_2$uns-penp (0.10 g, 0.37 mmol) in tetrahydrofuran under inert atmosphere. The resulting precipitate was collected, dried and dissolved in acetonitrile at 70 °C. The solution was filtered hot and brown crystals could be obtained by ether diffusion at –40 °C. Yield: 0.06 g (22 %). Anal.: $C_{80}H_{84}N_8B_2Cl_2Cr_2$ (1354.10); C 69.90 (calcd. 70.96); H 6.31 (6.25); N 8.97 (8.28) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 350 nm (3.1), 426 nm (2.8). **IR** (KBr): ν = 3052, 2994, 2983, 2833, 2370, 2309, 1945, 1881, 1816, 1677, 1607, 1579, 1478, 1439, 1424, 1288, 1266, 1160, 1097, 1054, 1030, 985, 845, 732, 706, 612 cm^{-1}.

[Cr(Me$_4$apme)Cl]Cl (3a)/[Cr(Me$_4$ampe)Cl$_3$] (3d): Anhydrous $CrCl_2$ (0.05 g, 0.40 mmol) and Me$_4$apme (bis(2-dimethyl-aminoethyl)(2-pyridylmethyl)amine) (0.10 g, 0.40 mmol) were stirred in tetrahydrofuran under inert atmosphere. The solution was stirred and a green precipitate occurred. The solid was collected, dissolved in a minimum of acetonitrile and filtered. During crystallization two species were obtained. Green crystals of **3d** were suitable for structural analysis (Figure 6). Brown crystals of **3a** were measurable, but refinement was not possible. Anal.: $C_{14}H_{26}N_4Cl_3Cr$ (408.74); C 41.00 (calcd. 41.14); H 6.24 (6.41); N 13.50 (13.71) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 366 nm (2.8), **IR** (KBr): ν = 3062, 3024, 2966, 2919, 1606, (1566), 1474, (1438), 1293, 1156, 1099, 1027, 934, 809, 773 cm^{-1}.

[Cr(Me$_4$apme)Cl]BPh$_4$ (3b): Anhydrous $CrCl_2$ (0.05 g, 0.40 mmol) and $NaBPh_4$ (0.14 g, 0.40 mmol) were stirred with Me$_4$apme (0.10 g, 0.40 mmol) in tetrahydrofuran under inert atmosphere. The resulting precipitate was collected, dried and dissolved in a minimum of acetonitrile at 70 °C. The solution was filtered hot and green crystals could be obtained by ether diffusion at –40 °C. Yield: 0.12 g (45 %). Anal.: $C_{38}H_{46}N_4BClCr$ (657.05); C 69.00 (calcd. 69.46); H 7.24 (7.06); N 8.58 (8.53) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 365 nm (2.8). **IR** (KBr): ν = 3052, 2998, 2982, 2965, 2366, 2309, 1941, 1892, 1817, 1606, 1577, 1475, 1437, 1427, 1300, 1265, 1155, 1090, 1052, 1022, 985, 930, 806, 770, 752, 734, 704, 609 cm^{-1}.

[Cr(Me$_6$tren)Cl]Cl (4a): Anhydrous $CrCl_2$ (0.05 g, 0.43 mmol) and Me$_6$tren (tris(2-dimethylaminoethyl)amine) (0.10 g, 0.43 mmol) were stirred in tetrahydrofuran under inert atmosphere. The resulting precipitate was collected, dried and dissolved in a minimum of acetonitrile. Light blue crystals were obtained by ether diffusion at –40 °C. Yield: 0.11 g (72 %). Anal.: $C_{12}H_{30}N_4Cl_2Cr$ (353.30); C 40.21 (calcd. 40.80); H 8.56 (8.56); N 15.39 (15.86) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 900 nm (2.3), **IR** (KBr): ν = 2970, 2895, 2427, 1637, 1560, 1469, 1289, 1174, 1100, 1018, 966, 933, 802, 772, 594, 492 cm^{-1}.

[Cr(Me$_6$tren)Cl]BPh$_4$ (4b): Anhydrous $CrCl_2$ (0.05 g, 0.43 mmol) and $NaBPh_4$ (0.15 g, 0.43 mmol) were stirred with Me$_6$tren (0.10 g, 0.43 mmol) in tetrahydrofuran under inert atmosphere. The resulting precipitate was collected, dried and dissolved in acetonitrile at 70 °C. The solution was filtered hot and green crystals could be obtained by ether diffusion at –40 °C. Yield: 0.09 g (33 %). Anal.: $C_{36}H_{50}N_4BClCr$ (637.07); C 66.22 (calcd. 67.87); H 7.68 (7.91); N 8.68 (8.79) %. **UV/Vis** (CH_3CN): λ_{max} (lg ε): 900 nm (2.3), **IR** (KBr): ν = 3054, 2999, 2981, 2892, 2839, 1958, 1891, 1822, 1579, 1474, 1466, 1428, 1348, 1286, 1266, 1244, 1173, 1133, 1098, 1038, 1017, 932, 897, 845, 802, 768, 734, 705, 611 cm^{-1}.

Oxidation of Toluene

The complexes (10 mg) were dissolved in acetone (0.7 mL) und the same quantity of toluene was added. Accordingly dioxygen was passed through the solutions (ca. 1 min). To determine the oxidation products and the yields after a reaction time of 7 d GC–MS measurements were conducted. Analysis of the toluene oxidation products were confirmed by comparison with the database (Spectral Database for Organic Compounds SDBS), specifically benzaldehyde. The yields of the product signals were calculated on the basis of comparisons to a calibration curve according to the internal standard xylene. Also control reactions with chromium(II) chloride and potassium dichromate were carried out and showed no reaction. And the blank only with acetone and toluene yielded no benzaldehyde.

X-ray Diffraction

The X-ray crystallographic data of **2b**, **3b** and **4a** were collected on a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved by direct methods in SHELXS97 and refined by using full-matrix least-squares in SHELXL97.[20] All hydrogen atoms were positioned geometrically and all non-hydrogen atoms were refined anisotropically.

The X-ray crystallographic data of **3d** was collected with a BRUKER NONIUS KappaCCD system using a BRUKER NONIUS. FR591 rotating anode as radiation source and an OXFORD CRYOSYSTEMS low temperature system. Mo-K_α radiation with wavelength 0.71073 Å and a graphite monochromator was used. The PLATON MULABS semi-empirical absorption correction using multiple scanned reflection was applied. The structure was solved by direct methods in SHELXS97 and refined with SHELXL97 using full-matrix least-squares.[20] All non-hydrogen atoms were refined anisotropically. Only the 50 % occupied hydrogen atoms were positioned geometrically.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-924632 for **1c**, CCDC-924633 for **2b**, CCDC-924634 for **3b** and CCDC-924635 for **4a** and CCDC-924636 for **3d**. Copies of the data can be obtained, free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic data for **2a** and **4b** are not deposited (see Supporting Information).

Supporting Information (see footnote on the first page of this article) Crystallographic data and selected bond lengths and angles of compounds of **1c**, **2a** and **4b**.

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