The First Structurally Characterized 4-Halo-2,5-Cyclohexadienone Transition Metal Complex

Udo Radius*[a] and Juri Attner[a]

Keywords: Coordination chemistry / Macrocyclic ligands / Calixarenes / Molybdenum / Tungsten

The calix[4]arene molybdenum imido complex [CaxO_4Mo(N*t*Bu)] (**1**) reacts with HCl to give, in a reversible reaction, the 1,2-addition product [Cax(OH)O_3Mo(N*t*Bu)Cl] (**4**). Reaction with $PhICl_2$ does not lead to scission of the imido group either, but results in an unprecedented 1,6-addition of chlorine to the metallocalixarene to give a molybdenum 4-chloro-2,5-cyclohexadienone complex [$Cax^{Cl}O_4$Mo(N*t*Bu)Cl] (**5**), which has been structurally characterized. This compound is the first example of a structurally characterized 4-halo-2,5-cyclohexadienone transition metal complex.

Introduction

Macrocyclic ligands have played an important role in the development of modern coordination chemistry and continue to do so.[1] Macrocyclic complexes are usually associated with high thermodynamic and kinetic stability and are therefore used as templates in supramolecular chemistry, in multi-component assembly processes, and as molecular receptors for guest molecules. Such ligands can act as spectator ligands for organometallic transformations at the metal atom.[2] However, in many cases, the ligands are also involved in the reaction processes. In metalloporphyrin chemistry, for example, reactions at the porphyrin periphery are quite common and these ligands are susceptible to redox processes and electrophilic as well as nucleophilic attack.[3]

Calix[4]arenes or calix[4]arene ethers,[4] with a pre-organized set of oxygen donor atoms in a quasi-planar arrangement, may be regarded as oxygen analogues of porphyrins and related nitrogen-containing macrocyclic ligands. These molecules have received considerable attention because of their host−guest chemistry and their ability to bind metals.[4,5] In the last few years, the potential of these types of ligands in organometallic and coordination chemistry has been clearly demonstrated. The simplest of the calixarenes, the calix[4]arene system, usually binds in a tetradentate fashion and retains its *cone*-like appearance.[5] In contrast to transition metal chemistry involving porphyrins, tetraazaannulenes, calixpyrroles, and related nitrogen donor ligands,[6] the calix[4]arene backbone is usually not involved in organometallic transformations.[7] Calix[4]arenes are therefore ideal co-ligands in transition metal chemistry, they tolerate acidic, basic, reductive, and oxidative conditions.

We report herein on a selective halogenation of the macrocyclic ligand in a metallocalix[4]arene through an unprecedented 1,6-chlorination. The resulting product represents the first isolated and structurally characterized 4-halo-2,5-cyclohexadienone complex.

Results and Discussion

As part of our program on molybdenum calix[4]arene complexes,[8] we have synthesized molybdenum imido complexes previously.[8b] The ultimate aim of this work was the synthesis of compounds of the general type [CaxO_4MoX_2] or [CaxO_4MoXX′] (Cax = hydrocarbon backbone of the *p*-*tert*-butylcalix[4]arene, $C_{44}H_{52}$; X = monoanionic ligand), which represent important starting materials for molybdenocalix[4]arene chemistry. Since the direct reaction of [$MoCl_5$] with *p*-*tert*-butylcalix[4]arene does not afford calix[4]arene molybdenum halides,[8a] we were led to investigate the reaction of [CaxO_4Mo(N*t*Bu)] (**1**) with HCl and Cl_2. Preliminary experiments revealed that a solution of [CaxO_4W(N*t*Bu)] (**2**) in dichloromethane reacts spontaneously with gaseous HCl at −20 °C to give the known calix[4]arene tungsten dichloro complex [CaxO_4WCl_2] (**3**).[7d]

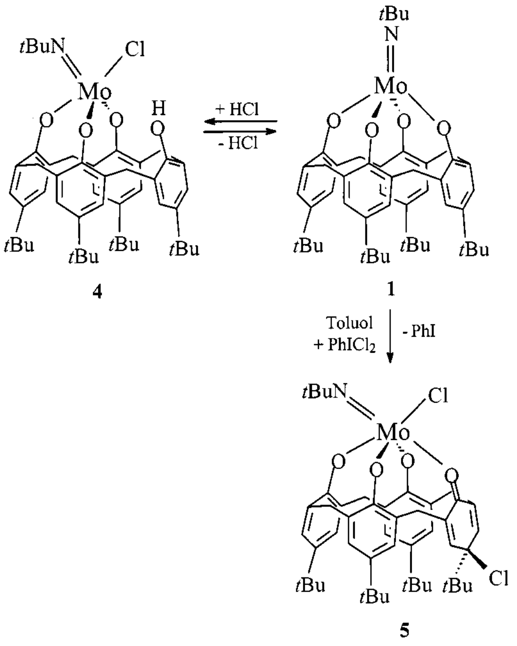
Whereas the imido ligand $[NR]^{2-}$ in **2** can be selectively replaced by two chloride ligands $[Cl]^-$, the reactivity of the analogous molybdenum compound **1** with respect to hydrochlorination is totally different (see Scheme 1). The reaction of **1** with one equivalent of HCl affords a dark-violet solution, which contains, according to NMR spectroscopy, a compound with local C_s symmetry of the calix[4]arene ligand, presumably [Cax(OH)O_3Mo(N*t*Bu)Cl] (**4**). The ^1H NMR spectrum of **4** features three signals due to the *t*Bu protons and three signals due to the protons of the methylene bridges, with relative integrals of 1:1:2. The signal of the OH proton can be detected at δ = 15.5. This low field

---

[a] Institut für Anorganische Chemie, Universität Karlsruhe (TH), Engesserstraße, Geb. 30.45, 76128 Karlsruhe, Germany
E-mail: uradius@achibm6.chemie.uni-karlsruhe.de

1434−1948/02/0101−0161 $ 17.50+.50/0

resonance is indicative of protonation at the basic oxygen atoms of the calix[4]arene ligand. Similarly downfield shifted signals have been detected previously, for example in $[\{Cax(OH)_2O_2Mo_2(OAc)_2\}(THF)]$, as reported by Lippard and co-workers.[9] However, the exact stereochemistry at the molybdenum center in **4** has not been established and protonation at the imido nitrogen atom cannot be totally excluded at present. We were not able to substitute the imido group, even by using a slight excess of HCl. The use of a larger amount of HCl in the reaction does not lead to scission of the imido group through proton transfer, but rather to decomposition of **4**. The protonated ligand $Cax(OH)_4$ was unequivocally detected in these reaction mixtures.



Scheme 1

Complex **4** decomposes to starting material **1** when solutions of this compound are concentrated in vacuo. The addition of HCl to **1** is totally reversible over several cycles. Reducing the pressure leads to elimination of HCl from **4**, and all attempts to remove **4** from equilibrium or to crystallize the complex have so far proved unsuccessful. Complex **4** could only be detected in solution and, as shown in Scheme 1, is the net result of a reversible 1,2-addition of HCl to the metal−oxygen bond of **1**.

The molybdenum imido function of **1** is similarly unreactive with respect to chlorine-transfer reagents. The addition of an equimolar amount of $PhICl_2$ to a solution of **1** in toluene causes a spontaneous color change of the reaction mixture to dark violet. After workup, the molybdenum complex $[Cax^{Cl}O_4Mo(NtBu)Cl]$ (**5**) could be isolated in good yield (see Scheme 1). Calix[4]arene $Cax(OH)_4$ does not react with $PhICl_2$ under comparable reaction conditions.

Spectroscopic data of the reaction product are in good agreement with an addition of Cl_2 to the imido compound **1**. The FD mass spectrum features a molecular peak at *m/z* = 885 (78%), which is the sum of the molar masses of **1** and Cl_2. The ^1H NMR spectrum of **5** shows a typical pattern for a pseudo-C_s-symmetric structure of the calix[4]arene ligand in solution. The resonance of the imido *t*Bu protons is detectable at $\delta = 1.44$, ca. 0.4 ppm further upfield than in the case of the starting compound **1**. The ^{13}C NMR spectrum features signals for quaternary carbon atoms with unusual shifts for calix[4]arene complexes, a resonance at $\delta = 42.5$, and a signal at $\delta = 191.2$. These signals can be attributed to a carbon atom of a *C*(*t*Bu)Cl group and to a carbonyl carbon atom, respectively. Furthermore, the infrared spectrum of **5** shows a strong band at 1668 cm^{-1} in the typical absorption region of carbonyl groups of α,β-unsaturated ketones.[10] These ^{13}C NMR and IR spectroscopic results suggest a 1,6-addition of chlorine to the molybdenum imido complex **1**, one chlorine atom being located at the metal atom and the other at the *para* position of one of the phenoxide units of the calix[4]arene ligand (see Scheme 1).

The result of an X-ray crystallographic study of crystals of **5** is shown in Figure 1 and confirms the structure proposed above. Complex **5** crystallizes in the monoclinic space group $P2_1/c$ with four formula units and four additional hexane molecules in the unit cell. The molybdenum atom is sixfold coordinated by four oxygen atoms O(1) to O(4), a nitrogen atom, and the chlorine atom Cl(1). Whereas the N−Mo−O(1) arrangement is almost linear with an angle of 176.2(15)°, the O(2)−Mo−O(4) and O(3)−Mo−Cl(1) angles of 159.6(12)° and 164.1(9)° demonstrate the distortion from an idealized octahedron. The molybdenum−oxygen distances to the oxygen atoms of the phenolate groups O(2), O(3), and O(4) are within the typ-

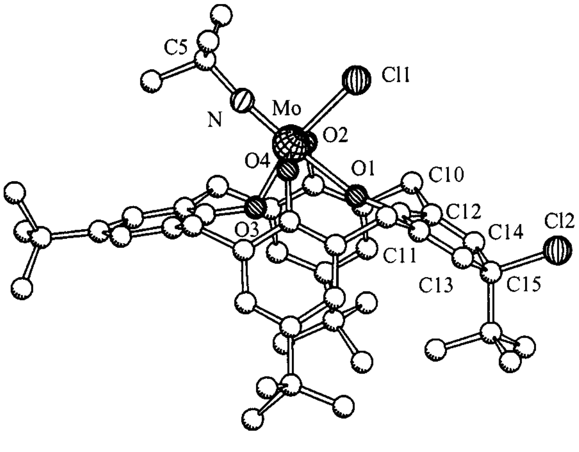


Figure 1. SCHAKAL plot of the molecular structure of $[Cax^{Cl}O_4$-$Mo(NtBu)Cl]$ **5**; hydrogen atoms are omitted for clarity and disorders of the *t*Bu groups are not resolved in the drawing; selected bond lengths [pm] and angles [°]: Mo−Cl(1): 241.0(1), Mo−N: 170.3(4), Mo−O(1): 216.0(3), Mo−O(2): 193.7(3), Mo−O(3): 191.9(3), Mo−O(4): 194.2(3), O(1)−C(10): 122.1(5), C(10)−C(11): 144.7(5), C(10)−C(12): 145.7(5), C(11)−C(13): 133.1(6), C(12)−C(14): 132.5(6), C(13)−C(15): 150.9(6), C(14)−C(15): 149.9(6), C(15)−Cl(2): 183.3(5), O(2)−C(20): 136.6(5), O(3)−C(30): 135.1(5), O(4)−C(40): 136.8(5); Mo−N−C(5): 173.0(4), Mo−O(1)−C(10): 163.1(3), Mo−O(2)−C(20): 125.3(2), Mo−O(3)−C(30): 119.6(3), Mo−O(4)−C(40): 124.6(2), N−Mo−O(1): 176.2(2), Cl(1)−Mo−O(3): 164.1(9), O(1)−Mo−O(3): 81.6(1), O(2)−Mo−O(4): 159.6(2)

ical range for molybdenum(VI) calix[4]arene complexes,[8] being between 191.9(3) pm and 194.2(3) pm; the Mo−Cl(1) distance of 241.0(1) pm is also unexceptional.[11] Interestingly, the molybdenum−nitrogen bond length to the imido ligand N atom of 170.3(4) pm is approximately 1.5 pm shorter than the Mo−N distance in the starting compound **1**, and the Mo−N−C(5) group is close to linear. These structural parameters are, as was likewise shown for **1**, in accordance with the triple bond character of the molybdenum−nitrogen bond.[12]

Significantly elongated with respect to the other molybdenum−oxygen bond lengths is the Mo−O(1) distance of 216.0(3) pm. This correlates with a short O(1)−C(10) contact of 122.1(5) pm, which is in the range for C=O double bonds.[13] The carbon atoms C(10) to C(15) of the carbon ring system connected to O(1) show alternating C−C bond lengths of 145.2(5) pm on average for C_{ipso}−$C_{ortho,}$ 132.8(6) pm for C_{ortho}−C_{meta}, and 150.4(6) pm for C_{meta}−C_{para}. This is in accordance with a description of the previously aromatic unit of the calix[4]arene as an α,β-unsaturated ring system. The C(15)−Cl(2) distance of 183.3(5) pm corresponds to a carbon−chlorine bond length involving an sp^3-hybridized carbon atom. As a net result, the structure of complex **5** in solution and in the solid state is best described as the 1,6-addition product of chlorine to **1**. To the best of our knowledge, no such selective 1,6-addition of chlorine to an organic or inorganic substrate has ever been observed previously.

Conclusion

The occurrence of electrophilic halogen attack in electrophilic aromatic substitution reactions,[14] especially on phenols,[15] is well-known. Such attack occurs in reactions in which a halogen atom replaces a substituent on the aromatic ring and the resulting kinetically unstable 4-halo-2,5-cyclohexadienone usually decomposes after the initial attack. If the starting phenol has a hydrogen atom in the *para* position, the dienone enolizes to the 4-halo product. With *p*-alkylphenols, the initial halogen attack leads to an "*ipso*-dienone". This can be used for further reactions, e.g. Diels−Alder reactions, or it can revert to the starting material through dehalogenation. 4-Alkyl-4-chloro-2,5-cyclohexadienones have previously been isolated by Fischer and Henderson.[16] Steroidal derivatives have been structurally characterized, as have related polyhalogenated compounds.[17] Calix[4]arene Cax(OH)$_4$ itself does not react with PhICl$_2$ under the reaction conditions that lead to **5**, giving an indication of the importance of the metal complex fragment coordinated at the calix[4]arene ligand in determining the outcome of the reaction.

The cyclohexadienone part of the macrocyclic ligand in **5** is the first example of a structurally characterized 4-halo-4-alkyl-2,5-cyclohexadienone in the coordination sphere of a transition metal complex. This moiety is stabilized by the highly Lewis acidic molybdenum(VI) complex fragment. After initial chlorine attack at the negatively charged and therefore activated ring system of the calix[4]arene ligand, the molecule does not regain its aromaticity but remains with an intact cyclohexadienone system, this being stabilized by attack of chlorine at the (positively charged) metal atom.

Experimental Section

General details were as given in our earlier reports.[8] Compounds **1** and **2** were prepared as described previously;[8b] PhICl$_2$ was prepared according to a published procedure.[18]

[CaxO$_4$WCl$_2$] (3) from [CaxO$_4$W(N*t*Bu)] (2): Gaseous HCl was for a short time passed into a solution of [CaxO$_4$W(N*t*Bu)] (**2**; 200 mg) in CH$_2$Cl$_2$ (20 mL), during which the color of the solution changed from yellow to dark red. After stirring for 5 min, all volatile materials were removed in vacuo. The main component of the remaining solid was identified as the known calix[4]arene tungsten complex [CaxO$_4$WCl$_2$] (**3**).[7d]

[Cax(OH)O$_3$Mo(N*t*Bu)Cl] (4): [CaxO$_4$Mo(N*t*Bu)] (**1**; 100 mg, 0.123 mmol) and pyHCl (14.0 mg, 0.123 mmol) were taken up in C$_6$D$_6$ (1.00 mL) in an NMR tube. The main species present in the resulting violet reaction mixture was identified by ^{1}H NMR spectroscopy as the addition product [Cax(OH)O$_3$Mo(N*t*Bu)Cl] (**4**). ^{1}H NMR (C$_6$D$_6$): δ = 0.69 [s, 18 H, C(CH$_3$)$_3$], 1.33 [s, 9 H, C(CH$_3$)$_3$], 1.35 [s, 9 H, C(CH$_3$)$_3$], 1.40 [s, 9 H, NC(CH$_3$)$_3$], 3.28 (d, $^2J_{H,H}$ = 13.9 Hz, 2 H, CH$_2$), 3.52 (d, $^2J_{H,H}$ = 14.7 Hz, 2 H, CH$_2$), 5.05 (d, $^2J_{H,H}$ = 14.5 Hz, 4 H, CH$_2$), 6.71 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Aryl-H$_m$), 6.91 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Aryl-H$_m$), 7.24 (s, 2 H, Aryl-H$_m$), 7.28 (s, 2 H, Aryl-H$_m$), 15.47 (br. s, 1 H, OH).

Evaporation of the volatiles from the solution led only to the starting material **1**. Compound **4** could also be obtained by the reaction of **1** with a stoichiometric amount of HCl in toluene or benzene.

[Cax^{Cl}O$_4$Mo(N*t*Bu)Cl] (5): A solution of [CaxO$_4$Mo(N*t*Bu)] (**1**; 800 mg, 0.99 mmol) in toluene (40 mL) was treated with PhICl$_2$ (271 mg, 0.99 mmol) and the resulting dark-violet solution was stirred for 8 h at room temperature. All volatile material was then removed in vacuo and the solid residue was extracted into hexane (60 mL). Removal of the solvent and drying in vacuo afforded **5** as a dark-violet solid; yield: 594 mg (68%). Crystals of **5** suitable for X-ray crystallography were obtained from saturated solutions of the compound in hexane. ^{1}H NMR (CDCl$_3$): δ = 1.02 [s, 9 H, C(CH$_3$)$_3$], 1.12 [s, 18 H, C(CH$_3$)$_3$], 1.33 [s, 9 H, C(CH$_3$)$_3$], 1.44 [s, 9 H, NC(CH$_3$)$_3$], 3.09 (d, $^2J_{H,H}$ = 13.2 Hz, 2 H, CH$_2$), 3.35 (d, $^2J_{H,H}$ = 14.6 Hz, 2 H, CH$_2$), 4.04 (d, $^2J_{H,H}$ = 13.2 Hz, 2 H, CH$_2$), 4.57 (d, $^2J_{H,H}$ = 14.6 Hz, 2 H, CH$_2$), 6.80 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Aryl-H$_m$), 7.02 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Aryl-H$_m$), 7.04 (s, 2 H, Aryl-H$_m$), 7.07 (s, 2 H, Aryl-H$_m$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 25.87 [*C*(CH$_3$)$_3$], 26.24, 28.62, 31.63 [C(*C*H$_3$)$_3$], 31.73 [*C*(CH$_3$)$_3$], 31.95 [C(*C*H$_3$)$_3$], 33.06 (CH$_2$), 34.06, 34.36 [*C*(CH$_3$)$_3$], 35.73 (CH$_2$), 42.52 [*C*(*t*Bu)Cl], 73.25 [N*C*(CH$_3$)$_3$], 124.42, 125.16, 126.46 (Aryl-C$_m$), 127.46, 127.56, 127.84, 139.89 (Aryl-C$_o$), 144.53, 144.88, 145.34 (Aryl-C$_p$), 148.08 (Aryl-C$_m$), 167.62, 168.33 (Aryl-C$_i$), 191.17 (Aryl-C=O). IR (KBr): ṽ = 1668 cm^{-1} [vs br, ν(C=O)]. FD-MS (10 kV): *m*/*z* (%) = 885 (78) [M + 2H]$^+$, 815 (31) [M + H − NC$_4$H$_9$]$^+$, 792 (100) [M − C$_4$H$_9$ − Cl]$^+$. EI-MS: *m*/*z* (%) = 847 (1) [M − Cl − H]$^+$, 813 (4) [M − 2Cl]$^+$, 791 (62) [M − Cl − C$_4$H$_9$]$^+$, 735 (27) [M − Cl − 2(C$_4$H$_9$)]$^+$. C$_{48}$H$_{61}$Cl$_2$NO$_4$Mo (882.9): calcd. C 65.30, H 6.96, N 1.59; found C 64.93, H 7.05, N 1.84.

X-ray Crystallographic Study: Data were collected on a Stoe-IPDS diffractometer (Ag-K_α radiation, λ = 0.56087 Å), T = 205(2) K;

data collection and refinement: SHELXS-97[19] and SHELXL-97,[20] monoclinic, space group $P2_1/c$; lattice constants a = 17.453(4), b = 13.199(3), c = 23.524(5) Å, β = 96.02(2)°; V = 5389.0(19) Å^3, Z = 4, μ(Ag-K_α) = 0.944 mm^{-1}, $2\Theta_{\max}$ = 39°; 9292 independent reflections measured, of which 6564 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 0.70 and −0.65 e/Å^3. 561 parameters (Mo, O, and N anisotropic; C anisotropic except disordered *t*Bu groups and solvent molecule; the positions of the H atoms were calculated for idealized positions); R_1 = 0.056; wR_2 = 0.1378.

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-163977. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We kindly thank Professor D. Fenske for his continuing support and interest in our work. A gift of metal chlorides from Fa. H. C. Starck GmbH, Goslar, is gratefully acknowledged.

---

[1] L. H. Gade, *Koordinationschemie*, Wiley-VCH, Weinheim, **1998**, chapters 1−3, 21.

[2] [2a] F. Vögtle, *Supramolekulare Chemie*, Wiley, Chichester, **1993**. [2b] J. M. Lehn, *Supramolekulare Chemie*, VCH Verlagsgesellschaft, Weinheim, **1995**. [2c] W. Kaim, B. Schwerdinski, *Bioanorganische Chemie*, Teubner, Stuttgart, **1995**. [2d] E. C. Constable, *Metal and Ligand Reactivity − An Introduction to the Organic Chemistry of Metal Complexes*, VCH Verlagsgesellschaft, Weinheim, **1996**.

[3] [3a] L. R. Milgram, *The Colours of Life − An Introduction to the Chemistry of Porphyrins and Related Compounds*, Oxford University Press, Oxford, **1997**. [3b] K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, **1975**. [3c] D. Dolphin, *The Porphyrins*, Academic Press, New York, **1978**. [3d] T. Mashiko, D. Dolphin, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, vol. 2, chapter 21.1.

[4] [4a] C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, **1989**. [4b] J. Vincens, V. Böhmer (Eds.), *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, **1991**. [4c] J. Vincens, Z. Asfari, J. M. Horrowfield (Eds.), *Calixarenes 50th Anniversary: Commemorative Issue*, Kluwer Academic Publishers, Dordrecht, **1994**. [4d] C. D. Gutsche, *Calixarenes Revisited*, Royal Society of Chemistry, Cambridge, **1998**. [4e] M. Lucinat, R. Ungaro (Eds.), *Calixarenes in Action*, Imperial College Press, London, **2000**. [4f] G. J. Lumetta, R. D. Rogers, A. S. Gopalan, *Calixarenes for Separations*, American Chemical Society, Washington D.C., **2000**.

[5] [5a] C. Floriani, *Chem. Eur. J.* **1999**, *5*, 19−23. [5b] C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93−161. [5c] D. M. Roundhill, *Prog. Inorg. Chem.* **1995**, *43*, 533−565.

[6] [6a] D. Mansuy, M. Lange, J. C. Chottard, J. F. Bartoli, B. Chevrier, R. Weiss, *Angew. Chem.* **1978**, *90*, 828−829; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 817−818. [6b] P. J. Brothers, J. P. Collman, *Acc. Chem. Res.* **1986**, *19*, 209−215. [6c] D. Mansuy, *Pure Appl. Chem.* **1987**, *59*, 759−770. [6d] F. Montanari, L. Casella, *Metalloporphyrin Catalyzed Oxidations*, Kluwer, Dordrecht, **1994**. [6e] H. Brand, J. Arnold, *Coord. Chem. Rev.* **1995**, *140*, 137. [6f] T. Aida, S. Inoue, *Acc. Chem. Res.* **1996**, *29*, 39−48. [6g] P. M. Jordan (Ed.), *Biosynthesis of Tetrapyrroles*, Elsevier, New York, **1991**. [6h] C. Floriani, *Chem. Commun.* **1996**, 1257−1263. [6i] P. A. Gale, J. L. Sessler, V. Kral, *Chem. Commun.* **1998**, 1−8. [6j] F. A. Cotton, J. Czuchajowska, *Polyhedron* **1990**, *9*, 2553−2566. [6k] P. Mountford, *Chem. Soc. Rev.* **1998**, *27*, 105−115.

[7] The scission of the *t*Bu groups or *ipso*-nitration reactions in *p*-*tert*-butylcalixarenes using Lewis acids under acidic conditions are well-known; see, for example: [7a] H. Kämmerer, G. Happel, V. Böhmer, D. Rathay, *Monatsh. Chem.* **1978**, *109*, 767−773. [7b] C. D. Gutsche, J. J. Levine, *J. Am. Chem. Soc.* **1982**, *104*, 2652−2653. [7c] O. Mogck, V. Böhmer, G. Ferguson, W. Vogt, *J. Chem. Soc., Perkin Trans. 1* **1996**, 1711−1715. A similar type of reaction has also been observed for a metallocalix[4]arene: [7d] F. Corazza, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Inorg. Chem.* **1991**, *30*, 4465−4468.

[8] [8a] U. Radius, J. Attner, *Eur. J. Inorg. Chem.* **1998**, 299−303. [8b] U. Radius, J. Attner, *Eur. J. Inorg. Chem.* **1999**, 2221−2231. [8c] J. Attner, U. Radius, *Chem. Eur. J.* **2001**, *7*, 783−790.

[9] [9a]J. Acho, S. J. Lippard, *Inorg. Chim. Acta* **1995**, *229*, 5−8. [9b] J. Acho, T. Ren, J. W. Yun, S. J. Lippard, *Inorg. Chem.* **1995**, *34*, 5226−5233.

[10] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, 3rd Edition, Thieme, Stuttgart, **1987**, 27−67.

[11] G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, *J. Chem. Soc., Dalton Trans.* **1989**, S1−S89.

[12] [12a] W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* **1980**, *31*, 123−175. [12b] D. E. Wigley, *Prog. Inorg. Chem.* **1994**, *42*, 239−482. [12c] W. A. Nugent, J. M. Mayer, *Metal−Ligand Multiple Bonds − The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*, Wiley, New York, **1988**.

[13] J. March, *Advanced Organic Chemistry*, 4th Edition, Wiley, NewYork, **1992**, p. 21.

[14] [14a] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanism*, 2nd edition, Plenum Press, New York, **1984**, chapter 9. [14b] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, Part B: Reactions and Synthesis*, 2nd edition, Plenum Press, New York, **1984**, chapter 8.1. [14c] H. R. Christen, F. Vögtle, *Grundlagen der Organischen Chemie*, 2nd edition, Otto Salle Verlag, Frankfurt/Main, **1989**, chapter 15. [14d] A. Streitwieser, C. H. Heathcock, E. M. Kosower, *Organische Chemie*, 2nd edition, VCH, Weinheim, **1994**, chapter 23. [14e] H. Beyer, W. Walter, W. Francke, *Lehrbuch der Organischen Chemie*, 23rd edition, S. Hirzel Verlag, Stuttgart, **1998**, chapter 5, especially 5.5. [14f] M. Sainsbury, *Aromatenchemie*, VCH, Weinheim, **1995**.

[15] [15a] J. H. P. Tyman, *Synthetic and Natural Phenols*, Elsevier, Amsterdam, **1996**. [15b] P. B. D. de la Mare, *Electrophilic Halogenation*, Cambridge University Press, Cambridge, **1976**. [15c] P. B. D. de la Mare, *Acc. Chem. Res.* **1974**, *7*, 361−368.

[16] [16a] A. Fischer, G. N. Henderson, *Can. J. Chem.* **1979**, *57*, 552−557. [16b] A. Fischer, G. N. Henderson, *Can. J. Chem.* **1983**, *61*, 1045−1052.

[17] [17a] F. Mukawa, *J. Chem. Soc., Perkin Trans. 1* **1988**, 457−460. [17b] A. M. Soerensen, B. Jerslev, *Acta Chem. Scand.* **1968**, *22*, 319−327.

[18] H. J. Lucas, E. R. Kennedy, *Org. Synth.*, Wiley, New York, **1955**, *3*, 482−483.

[19] G. M. Sheldrick, *SHELXS-97: Program for Crystal Structure Solution*, Universität Göttingen, **1997**.

[20] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, Universität Göttingen, **1997**.

Received August 3, 2001
[I01287]