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One step substitution of NO and Cl by a metal-S-C-N-ring in $CpCr(NO)_2Cl$: synthesis and molecular structure of $CpCr(NO)$'DMPYS' ($Cp = \pi$-C_5H_5; DMPYS = 4,6-dimethyl-pyrimidine-2-thiolato)

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Dedicated to Professor Jörn Müller for his 65th birthday

Abstract

$CpCr(NO)_2Cl$ reacts in THF under reflux with the Na salt of 4,6-dimethyl-pyrimidin-2-thiol to give $CpCr(NO)(DMPYS)\cdot 1/4$ toluene ($Cp = \pi$-C_5H_5; DMPYS = 4,6-dimethylpyrimidine-2-thiolato) and NaCl. The ligand substitution in $CpCr(NO)_2Cl$ probably occurs over displacement of NO followed by Cl^- elimination. $CpCr(NO)$'DMPYS' crystallizes in the triclinic space group $P\bar{1}$, formally with 25% of a toluene solvate molecule for each $CpCr(NO)(DMPYS)$-unity. In the new complex, the chromium atom shows a 'tetrahedral' coordination geometry derived from the octahedral structural principle, with a four members ring formed by the metal atom and the fragment S–C–N of the ligand. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitrosyl complexes; Substitution in nitrosyl complexes; NO-complexes of chromium; Thiolato complexes of chromium

1. Introduction

The extensive and rich chemistry developed around substitution reactions in nitrosyl complexes and particularly in $CpCr(NO)_2Cl$ is very interesting for many reasons. Early works had been shown [1] that in spite of the strong π-acceptor character of the nitrosyl ligand in metal–NO complexes and the remarkably stable metal–nitrogen-backbonding, reactions of $CpCr(NO)_2Cl$ with donor ligands like piperazine, pyridine, triphenylphosphine and many others, lead to the formation of neutral $CpCr(NO)LCl$ complexes, instead to cationic compounds [2] of the type $[CpCr(NO)_2L]Cl$. This means that one NO group, and not the Cl ligand undergoes substitution, in a first step. A classical example of Cl^- displacement [3] with formation of a cationic complex represents the reaction of $CpCr(NO)_2Cl$ with CO under pressure (300 atm), in the presence of the Friedel–Krafts catalyst $AlCl_3$. The complex salt $[CpCr(NO)_2CO]PF_6$ was isolated (and characterized) by hydrolysis of $[CpCr(NO)_2CO]AlCl_4$ with NH_4PF_6. Therefore, a direct substitution of the Cl ligand in $CpCr(NO)_2Cl$ seems to be strongly dependent on the ligand type and requires at first sight very energetic reaction conditions.

In correlation with these assignments we report the substitution of one NO group and the chloride ion in $CpCr(NO)_2Cl$ by a donor, bidentate anionic ligand, and the synthesis of neutral disubstituted $CpCr(NO)$DMPYS (DMPYS = 4,6-dimethyl-pyrimidine-2-thiolato). The X-ray structural characterization of the new complex will be also discussed.

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2. Experimental

All manipulations, including the chromatographic proceeding, were conducted under argon by use of standard Schlenk techniques. The solvents were dried with sodium/benzophenone and distilled before use. SiO_2 was dried under high-vacuum at 160 °C for 3 h. $CpCr(NO)_2Cl$ was obtained according to reported procedures [1]. 4,6-dimethyl-pyrimidine-2-S^-Na^+ was prepared by equimolar reaction of 4,6-dimethyl-pyrimidine-2-thiol with NaH in THF at −10 °C.

2.1. (η^5-Cyclopentadienyl)-nitrosyl-(4,6-dimethylpyrimidine-2-thiolato)-chromium (II), CpCr(NO)(DMPYS)·1/4 toluene

In a 100-ml two necked flask equipped with an argon inlet and stirring bar, 0.212 g (1 mmol) of $CpCr(NO)_2Cl$ was dissolved in 35 ml of THF. After addition of 0.163 g (1 mmol) of sodium 4,6-dimethyl-pyrimidine-2-thiolate in 45 ml of THF under stirring, the dark-green solution turned slowly dark-brown. The reaction mixture was refluxed for 10 h. After filtration the solvent was removed under vacuum up to a minimum volume of solution and the residue was chromatographed on SiO_2 (70–230 ASTM). Two little zones were eluted, with hexane and with a mixture of 70% hexane and 30% THF, respectively, a first one yellow, containing unreacted ligand, and a second green zone, containing the parent complex. A third, wide amber-colored zone affords the product and was eluted with hexane–THF 1:1; the solvent was removed under reduced pressure and the residue was dissolved in toluene and recrystallized from this solvent at −18 °C. A quite small quantity of a crystalline solid isolated in the filtration was identified also by means of X-ray diffractometry as being the dithiolate R–S–S–R (R = 4,6-dimethyl-pyrimidyl-2), probable oxidation product of 4,6-dimethyl-pyrimidine-2-S^-Na^+.

Proprieties: reddish-brown, crystalline air sensitive substance; $C_{11}H_{12}CrN_3OS\cdot 1/4\ C_7H_8$ (309.332). Yield, 72% based on $CpCr(NO)_2Cl$ taken.

3. Results and discussion

X-ray diffraction studies of CpCr(NO)(DMPYS)·1/4 toluene were performed with an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo–K_α radiation at −70 °C. Crystal data and experimental conditions are given in Table 1. The structure has been solved using direct methods [4] and difference Fourier techniques, refined by a full-matrix least squares procedure on F^2 [5]. Numerical absorption corrections were applied [6]. Anisotropic displacement parameters were used to refine the position of the non-hydrogen atoms of the metal complex, the toluene atoms were isotropically refined. The hydrogen atoms of toluene were not considered. Scattering factors and anomalous dispersion corrections have been taken from International Tables for Crystallography [7]. Most calculations have been performed using the programs HELENA [8] and SHELXL 97 [5], as well graphical representations by ORTEP 3 [9].

Table 1
Crystal data and structure refinement parameters of CpCr(NO)(DMPYS)·toluene

Empirical formula	$C_{11}H_{12}CrN_3OS.\cdot 0.25(C_7H_8)$
Formula weight	309.332
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	7.6139(7)
b (Å)	13.1099(14)
c (Å)	14.5868(15)
α (°)	90.276(13)
β (°)	96.049(12)
γ (°)	104.826(12)
V(Å^3)	1398.9(2)
Z	4
D_{calc} (g cm^{-3})	1.4688(2)
Radiation λ (Å)	Mo–K_α, 0.71073
μ (mm^{-1})	0.960
Absorption correction	Numerical correction (faces indexed analytical)
T_{min}/T_{max}	0.9008/0.9516
Color/crystal size (mm)	Yellow/0.07 × 0.15 × 0.20
θ/°/index ranges	2.1, 27.97/−9, 9; −17, 16; −19, 19
Reflections collected/parameters	13 464/342
Independent reflections/R_{int}	6209/0.0895
Reflections observed, $I > 2s(I)$	2917
Goodness-of-fit on F^2	0.794
R_1/wR_2	0.0486/0.1109

In the X-ray measures of [CpCr(NO)(DMPYS)·1/4 toluene], space group $P\bar{1}$ was chosen on the basis of statistics and later justified by the successful refinement. The asymmetric unit contains two crystallographically independent CpCr(NO)(DMPYS) complexes and 1/2 toluene which is disordered about the inversion center at (0.5, 0, 0). Three different orientations were refined but only for one of them the exocyclic methyl group could be localized. The two independent [CpCr(NO)(DMPYS)]-units form two monomeric structures which are related with the two others halves of the cell through a crystallographic inversion center. The distance between the middle of the plane of the cyclopentadienyl ring and the Cr-atom (centroid) is 1.884 Å. An ellipsoid representation of the molecular structure of the complex is shown in Fig. 1. Selected bond lengths and angles are given in Table 2.

Preliminary reactions of $CpCr(NO)_2Cl$ with DMPYS**H** had shown that the displacement of one

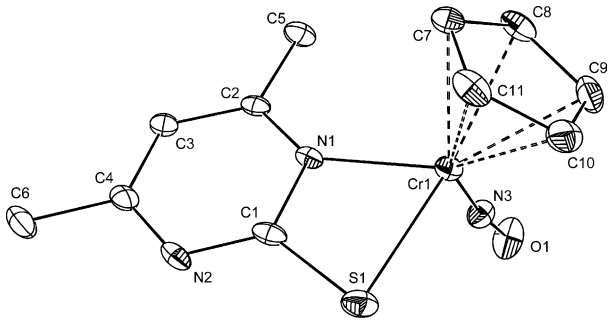

Fig. 1. ORTEP 3 [9] representation of the molecular structure of CpCr(NO)(DMPYS)·1/4 toluene. Thermal ellipsoids represent 30% probability. Hydrogen atoms and toluene groups are omitted by clarity.

Table 2
Selected bond lengths (Å) and angles (°) for CpCr(NO)(DMPYS)·toluene

Bond lengths			
Cr(1)–C(7)	2.239(4)	C(4)–C(6)	1.503(6)
Cr(1)–C(8)	2.208(4)	C(7)–C(8)	1.405(7)
Cr(1)–C(9)	2.219(4)	C(7)–C(11)	1.384(7)
Cr(1)–C(10)	2.234(5)	C(8)–C(9)	1.413(7)
Cr(1)–C(11)	2.254(5)	C(9)–C(10)	1.402(7)
Cr(1)–S(1)	2.413(14)	C(10)–C(11)	1.417(7)
Cr(1)–N(1)	2.032(3)	N(1)–C(1)	1.370(5)
Cr(1)–N(3)	1.676(4)	N(1)–C(2)	1.333(5)
O(1)–N(3)	1.203(5)	N(2)–C(1)	1.334(5)
C(3)–C(4)	1.390(6)	N(2)–C(4)	1.350(6)
Bond angles			
N(1)–Cr(1)–N(3)	97.99(16)	N(1)–C(1)–S(1)	110.5(3)
C(8)–Cr(1)–S(1)	153.12(14)	N(1)–C(1)–N(2)	124.9(4)
C(7)–Cr(1)–N(1)	90.87(15)	N(2)–C(4)–C(3)	122.2(4)
C(9)–Cr(1)–N(3)	95.35(19)	C(2)–C(3)–C(4)	119.1(4)
Cr(1)–N(1)–C(1)	101.5(3)	C(3)–C(2)–C(5)	123.2(4)
Cr(1)–S(1)–C(1)	78.18(15)	C(3)–C(4)–C(6)	121.7(4)
Cr(1)–N(3)–O(1)	173.7(3)	C(8)–C(7)–C(11)	109.4(4)

NO group in $CpCr(NO)_2Cl$, by refluxing a THF solution of the complex with the ligand does not occur. Even in the presence of a base like triethylamine (Et_3N) the reflux of the mixture does not make feasible the deprotonation of DMPYSH, with subsequent nucleophilic substitution of the chlorine ligand by the thiolato-anion $DMPYS^-$, since the formation of $Et_3NH^+Cl^-$-observed in others reactions [10,11] carried out in the presence of Et_3N and in which the deprotonation is attained to Cl^- elimination—does not take place.

From the reaction of $DMPYS^-Na^+$ with $CpCr(NO)_2Cl$ under driving conditions we had expected the formation of a neutral compound, however, the bidentate ability of the anionic ligand does not surprise, since according the literature [1,2], and as already referred to, in $CpCr(NO)_2Cl$ the abstraction of the Cl ligand is not preferable, and when it takes place this means that one NO molecule was already displaced. A probable reaction pathway leads initially, over nucleophilic attack from the bigger 'side' of the ligand anion-molecule—the S-atom—to the displacement of one NO group. To maintenance of the oxidation state of the metal atom and to keep the charge balance of the solution, the Cl anion is then displaced of the coordination sphere of the Cr-atom and substituted by a coordinating N-atom of the ligand.

The $\overline{\text{Metal–S–C–N}}$-ring occurs only in tree (reported) compounds, two of them being complexes of bidentate 2-mercaptopyridine-*N*,*S*: bis(η^5-Cyclopentadienyl)-(2-mercaptopyridyl-*N*,*S*)-molybdenumhexafluoro-phosphate [12] and dicarbonyl-(η^5-cyclopentadienyl)-(2-thiopyridine-*N*,*S*)-molybdenum [13]. Unique case, however, of a $\overline{\text{Me–S–C–N}}$-bond reported in the literature with the same ligand employed in this work is that of bis(η^5-cyclopentadienyl)-methyl-(4,6-dimethylpyrimidine-2-thiolato)-zirconium, described by Fandos et al. [14].

There are only four compounds derived from reactions of $CpCr(NO)_2Cl$ with thio-ligands, and all of them show the ability of this ligand type to act as bridge-forming ligand, like the classical *trans*-bis(μ_2-Phenylthio)-dinitrosyl-bis-(η^5-cyclopentadienyl)-di-chromium [15] and the $(t\text{-}C_4H_9S)^-$ derivatives (μ_2-*t*-Butyldisulfonyl)-(μ_2-*t*-butylthiolato)-bis(η^5-cyclopentadienyl) -dinitrosyl-di-chromium [16], (μ_2-*t*-Butylthiolato)-(μ_2-chloro)-bis(η^5-cyclopentadienyl)-nitroso-chromium) [17], and bis (μ_2-*t*-Butylthiolato)-(μ_2-methylthiolato)-bis(η^5-cyclopentadienyl)-di-chromium trifluoromethanesulfonate [18]. All the binuclear complexes present Cr–Cr-bonds, with the anion *t*-butylthiolato (or more than one) acting as μ_2-ligand; interesting is the fact that in the mentioned complexes (with exception of the last structure) each metal-atom retains one NO group and one π-bonding Cp-ring of the parent complex, any of them being formed by the association—via ligands—of two $[CpCrNO]^+$-fragments, 'building' unity of so many structurally analogous binuclear nitrosyl complexes of chromium, like $[CpCr(NO)_2]_2$ [19], $Cp_2Cr_2(NO)_3NOHtBu$ or $Cp_2Cr_2(NO)_3NHR$ ($R = CH_3$, $n\text{-}C_4H_9$) [20].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 181305. Copies of this informations may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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