

η^3 -1,3,5-Triazacyclohexane complexes of tribenzylchromium(III) [☆]

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Abstract

1,3,5-Tribenzyl-1,3,5-triazacyclohexane ('Bz₃TAC') and 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane ('Cy₃TAC') react with CrCl₃(THF)₃ to the corresponding complexes (Bz₃TAC)CrCl₃ (**1a**) and (Cy₃TAC)CrCl₃ (**1b**). These react with benzyl sodium in toluene to the tribenzylchromium(III) complexes (Bz₃TAC)Cr(CH₂Ph)₃ (**2a**) and (Cy₃TAC)Cr(CH₂Ph)₃ (**2b**). The crystal and molecular structure of **2b** · 1.5 toluene has been determined by X-ray diffraction.

Keywords: Chromium; Benzyl; 1,3,5-Triazacyclohexane; UV-vis absorption spectroscopy; NMR spectroscopy; IR spectroscopy

1. Introduction

Compared to the extensive work on homogeneous coordination compounds of the early transition metals that catalyze Ziegler–Natta-type olefin polymerization, only a few chromium-based compounds have been made as homogeneous model systems for the Phillips catalysts. Theopold et al. [1] prepared a few well-characterized Cp^{*}-chromium alkyl complexes, e.g. [Cp^{*}Cr(CH₂Ph)₃Li], that are able to polymerize ethylene. However, the original Phillips catalyst is based on a chromium alkyl (or hydride) in the hard ligand sphere of the silicate oxygen atoms (e.g. Ref. [2]) and recently Flood et al. [3] have shown that cationic rhodium(III) methyl complexes containing the hard 1,4,7-trimethyl-1,4,7-triazacyclononane ligand are able to catalyze slow ethylene polymerization even in water. Therefore, we are investigating alkyl chromium complexes in a hard ligand environment of tertiary nitrogen donors.

Recently, we have shown that the much more readily accessible 1,3,5-triazacyclohexane R₃TAC (R = Me, ⁱPr) can be used instead of 1,4,7-triazacyclononanes to prepare η^3 -bonded chromium trichloride complexes [4]. Two crystal structures of the η^3 -bonded ligands showed

that the bite angle N—M—N (62°) is much smaller than in 1,4,7-triazacyclononane complexes, which should further increase the reactivity of these complexes. (ⁱPr₃TAC)CrCl₃ could be converted to the bis-alkyl complex (ⁱPr₂TAC)CrCl(CH₂SiMe₃)₂. However, we were unable to prepare the corresponding tris-alkyl compounds using lithium reagents. Apparently, the barely soluble chromium trichloride complexes reacted with the large excess of the soluble lithium alkyls with reduction to lower valent chromium compounds that could not be characterized.

In this paper we describe the syntheses of more soluble 1,3,5-triazacyclohexane complexes of chromium trichloride and their trialkylation with the barely soluble benzyl sodium.

2. Results

In a similar manner to Me₃TAC and ⁱPr₃TAC [4], Bz₃TAC and Cy₃TAC react with CrCl₃(THF)₃ in THF to yield the corresponding purple (R₃TAC)CrCl₃ [R = Bz (**1a**) and Cy (**1b**)]. However, they are much more soluble in chlorinated solvents (up to 6 g l⁻¹ of **1a** and 0.6 g l⁻¹ of **1b** in CH₂Cl₂). Complex **1a** shows some solubility even in THF and must be precipitated by addition of water. The compounds are air- and water-stable and do not decompose below 350°C.

UV-vis spectra of **1a**, **b** in CH₂Cl₂ show the first two absorptions corresponding to the octahedral Cr^{III}

[☆] Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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d–d transitions $A_{2g} \rightarrow T_{2g}$ and $A_{2g} \rightarrow T_{1g}(F)$. The average ligand field parameters $10Dq(\mathbf{1a}) = 13\,989\text{ cm}^{-1}$, $10Dq(\mathbf{1b}) = 13\,651\text{ cm}^{-1}$, $B'(\mathbf{1a}) = 570\text{ cm}^{-1}$ and $B'(\mathbf{1b}) = 550\text{ cm}^{-1}$ can be derived. A third transition corresponding to $A_{2g} \rightarrow T_{1g}(P)$ was found as a shoulder at $29\,917\text{ cm}^{-1}$ for $\mathbf{1a}$ and $27\,400\text{ cm}^{-1}$ for $\mathbf{1b}$ close to the value calculated from Dq and B' ($30\,840$ and $30\,070\text{ cm}^{-1}$). With the ligand field parameters for $[\text{CrCl}_6]^{3-}$ and $[\text{Cr}(\text{en})_3]^{3+}$, an average $10Dq \approx 17\,500\text{ cm}^{-1}$ and $B' \approx 600\text{ cm}^{-1}$ can be expected for $(\text{amine})_3\text{CrCl}_3$. This shows that $R_3\text{TAC}$ causes a much weaker ligand field splitting and a smaller Racah parameter B' than normal amine ligands.

Stirring $\mathbf{1a, b}$ with yellow NaCH_2Ph slowly produced brown solutions of $(R_3\text{TAC})\text{Cr}(\text{CH}_2\text{Ph})_3(\mathbf{2a, b})$ which can be recrystallized from toluene (see Scheme 1).

The elemental analyses were low in carbon corresponding to up to three carbon atoms less per chromium. This could be improved by addition of KNO_3 to the sample to allow better combustion.

UV–vis spectra of $\mathbf{2a, b}$ show two absorptions that can be assigned to the d–d transitions as for $\mathbf{1a, b}$ giving the ligand field parameters $10Dq(\mathbf{2a}) = 15\,822\text{ cm}^{-1}$, $10Dq(\mathbf{2b}) = 15\,820\text{ cm}^{-1}$, $B'(\mathbf{2a}) = 670\text{ cm}^{-1}$, and $B'(\mathbf{2b}) = 470\text{ cm}^{-1}$. As expected, the $10Dq$ value is increased by alkylation. These spectra can be compared to the reported UV–vis spectra of $[\text{Cp}^*\text{Cr}(\text{CH}_2\text{Ph})_3]^-$ and $[\text{Cp}^*\text{Cr}(\text{CH}_2\text{Ph})_3\text{Li}]$ [1]. When assigned to d–d transitions, $10Dq = 15\,800$ and $16\,600\text{ cm}^{-1}$ and $B' = 200$ and 180 cm^{-1} , respectively, can be obtained. This shows that the ligand field splitting caused by Cp^* is similar to $R_3\text{TAC}$, but B' is much smaller due to the more covalently bound Cp^* .

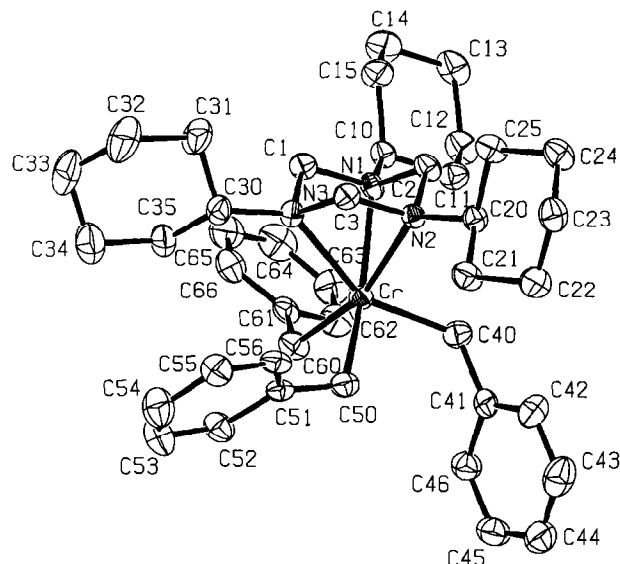
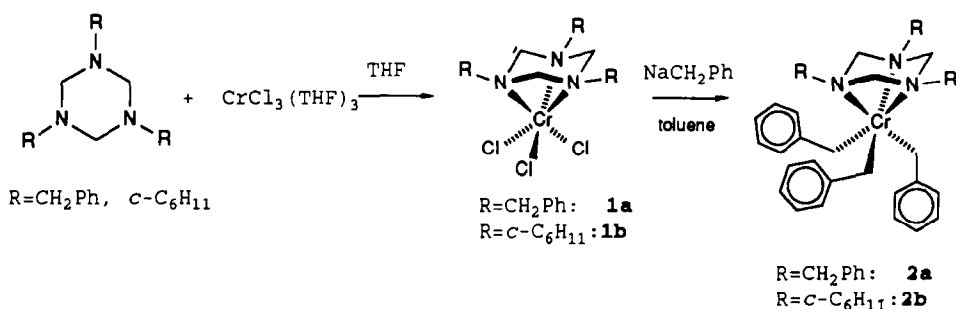


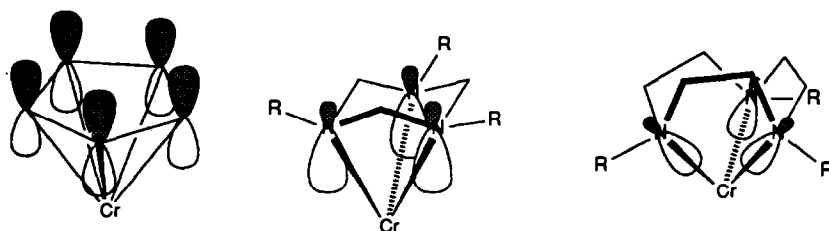
Fig. 1. Platon plot of $\mathbf{2b} \cdot 1.5\text{toluene}$.

The presence of the Cr–benzyl groups can also be seen in the IR spectra. Comparing $(R_3\text{TAC})\text{CrCl}_3$ with $(R_3\text{TAC})\text{Cr}(\text{CH}_2\text{Ph})_3$ allows the assignment of four characteristic absorptions to the Cr–benzyl groups, 3062 , 1588 , 1483 , 961 cm^{-1} for $\mathbf{2a}$ and 3063 , 1591 , 1481 , 966 cm^{-1} for $\mathbf{2b}$, which compare well with the vibrations in $[\text{Cp}^*\text{Cr}(\text{CH}_2\text{Ph})_3\text{Li}]$ that are shifted upon full deuteration of the benzyl group (3057 , 1589 , 1477 , 966 cm^{-1}) [1].

The X-ray crystal structure of $\mathbf{2b}$ (Fig. 1) shows monomeric complexes with one η^3 -bound C_3TAC and three benzyl groups. The average Cr–C bond length of



Scheme 1.



Scheme 2. Comparison of the donor orbital overlap in Cp , $R_3\text{TAC}$ and $R_3\text{TACN}$.

2.12 Å and the C—Cr—C angles of 90°–97° are similar to the distances and angles in [Cp*Cr(CH₂Ph)₂(py)] or [Cp*Cr(CH₂Ph)₃Li] (2.12–2.17 Å, 93°–100°) [1]. However, the long Cr—N bonds (av. 2.28 Å) and acute N—Cr—N angles of 61°–62° are similar to the distances and angles in the only other structurally characterized triazacyclohexane complex of Cr^{III}, (iPr₃TAC)CrCl(CH₂SiMe₃)₂ (229–230 Å *trans* to C, 60°–63°), and result from the ring strain [4]. Since the triazacyclohexane ligand shows no severe distortions, the nitrogen lone pairs are oriented essentially parallel to each other and cannot overlap with chromium orbitals as well as other amine ligands. This situation is more comparable to Cp ligands where the metal-bonding p-orbitals are also parallel to each other. In fact, the cone angle of the donor atoms of the Cp* in [Cp*Cr(CH₂Ph)₃Li] is 32° [1] compared to 36° in **2b** and a much larger 49° in the triazacyclononane complex (tBu₃TACN)CrCl₃ [5]. Consequently, the Cr—C(Cp*) bond is similarly elongated to 2.29 Å (see Scheme 2).

In conclusion, we have demonstrated that chromium tribenzyl complexes in the hard ligand environment of 1,3,5-triazacyclohexanes can be prepared which show many similarities to [Cp*Cr(CH₂Ph)₃]⁻.

3. Experimental details

All manipulations were carried out under argon (standard vacuum line, Braun glove box) and using Schlenk techniques. Solvents were dried according to standard methods. Bz₃TAC was purchased from Aldrich and recrystallized from hexane. Cy₃TAC has been prepared before [6]. CrCl₃(THF)₃ [7] and NaCH₂Ph (analogous to KCH₂Ph [8]) were prepared according to published procedures. For IR spectra a Perkin-Elmer 580 B instrument, for UV-vis spectra a Beckman DU 650 instrument, for ¹H NMR spectra a Bruker WP-80 SY (80 MHz) instrument and for ¹³C NMR spectra a Bruker ARX 200 (200 MHz) instrument were used. Elemental analyses were performed on a Perkin-Elmer Series II CHN/O analyser 2400 or at the analytical facility of the Humboldt Universität, Berlin. Melting points were determined on a HWS-SG 2000 instrument and are uncorrected. Magnetic moments are determined according to the Evans method [9].

3.1. Synthesis of Cy₃TAC

Sodium hydroxide (1 g) and then cyclohexylamine (24 ml, 210 mmol) were added to a 37% solution of formaldehyde in water (20 ml, 269 mmol). After 30-min stirring, the organic phase was separated and the aqueous phase extracted three times with 30 ml of Et₂O. After drying the combined organic phases with NaOH and removal of the solvent in vacuo, the crude Cy₃TAC

was recrystallized repeatedly from hexane until a melting point of 72.5°C (lit. value [6]: 72.2–72.8°C) was obtained. Yield, 14.6 g (63%). Anal. Calc. for C₂₁H₃₉N₃ (333.56): C, 75.62; H, 11.79; N, 12.60%. Found: C, 74.92; H, 11.50; N, 13.08%. ¹H NMR (CDCl₃) δ: 3.59 (br s, 2H, N—CH₂—N); 2.98 (br s, 4H, N—CH₂—N); 2.67 (m, 2H, N—CH); 2.45 (m, 1H, N—CH); 1.59–1.93 and 1.06–1.35 (m, 30H, Cy) ppm. ¹³C NMR (CDCl₃) δ: 68.39 (N—CH₂—N); 58.54 (N—CH); 30.04, 26.28, 25.80 (Cy) ppm.

3.2. Synthesis of (Bz₃TAC)CrCl₃ (**1a**)

Bz₃TAC (630 mg, 1.76 mmol) and CrCl₃(THF)₃ (644 mg, 1.72 mmol) were stirred in THF (20 ml). After 1 h, 100 ml of water were added to the purple suspension for complete precipitation of the product. Filtration, repeated washings with water and then Et₂O, and drying in vacuo yielded 360 mg (97%) of purple **1a**, m.p. > 400°C. Anal. Calc. for C₂₄H₂₇N₃CrCl₃ (515.86): C, 55.88; H, 5.28; N, 8.15%. Found: C, 55.44; H, 5.19; N, 8.17%. IR (KBr) ν (cm⁻¹): 410(w); 419(m); 465(w); 470(w); 511(s); 618(m); 701(s); 747(s); 756(s); 768(w); 912(m); 921(s); 973(m); 1003(w); 1018(s); 1030(m); 1053(m); 1071(s); 1081(s); 1092(s); 1114(w); 1132(s); 1153(s); 1203(w); 1218(m); 1260(w); 1278(w); 1297(m); 1336(w); 1347(m); 1366(s); 1412(m); 1456(s); 1496(m); 2878(m); 2921(w); 2946(m); 3005(w); 3033(m); 3063(w); 3089(w); 3107(w). μ_{eff} = 3.8 μ_B. UV-vis (CH₂Cl₂) ν (cm⁻¹) (ε, l mol⁻¹ cm⁻¹): 13 989 (160); 19 650 (330); 29 917 (30).

3.3. Synthesis of (Cy₃TAC)CrCl₃ (**1b**)

Cy₃TAC (2.00 g, 6.00 mmol) and CrCl₃(THF)₃ (2.02 g, 5.39 mmol) were stirred in THF (30 ml) for 1 h. Filtration, repeated washings with Et₂O and drying in vacuo yielded 2.37 g (89%) of purple **1b**, m.p. 360°C (dec.). Analysis: Calc. for C₂₄H₂₇N₃CrCl₃ (491.92): C, 51.27; H, 7.99; N, 8.54%. Found: C, 51.04; H, 7.81; N, 9.16%. IR (KBr) ν (cm⁻¹): 404(m); 519(w); 547(m); 842(w); 897(w); 918(m); 948(s); 987(m); 1016(s); 1033(m); 1054(m); 1067(s); 1078(s); 1093(s); 1120(s); 1151(w); 1170(s); 1201(m); 1211(w); 1261(m); 1280(m); 1292(w); 1314(w); 1338(w); 1353(m); 1381(m); 1396(w); 1406(w); 1453(s); 1484(w); 2857(s); 2930(s); 2970(w); 2997(w). UV-vis (CH₂Cl₂) ν (cm⁻¹) (ε, l mol⁻¹ cm⁻¹): 13 651 (130); 19 145 (230); 27 400 (50).

3.4. Synthesis of (Bz₃TAC)Cr(CH₂Ph)₃ (**2a**)

Benzyl sodium (200 mg, 1.75 mmol) and **1a** (214 mg, 0.415 mmol) were stirred in toluene (20 ml) for 5 d. After allowing the mixture to settle for 1 d, the deep brown solution was decanted from the yellow residue.

Evaporation of the solvent and drying in vacuo yielded 161 mg (57%) of brown **2a**, m.p. 143–145°C. Anal. Calc. for $C_{45}H_{48}N_3Cr$ (682.90): C, 79.15; H, 7.09; N, 6.15%. Found: C, 73.99; H, 7.56; N, 6.31%. IR (KBr) ν (cm^{-1}): 437(w); 464(w); 505(m); 614(w); 651(w); 698(s); 754(s); 961(m); 1019(m); 1072(m); 1084(s); 1093(m); 1130(m); 1202(m); 1212(m); 1309(m); 1346(m); 1454(s); 1483(s); 1495(s); 1588(s); 1653(w); 1675(m); 1703(s); 2824(w); 2933(w); 2984(m); 3008(w); 3027(m); 3062(m); 3085(w); 3106(w). UV-vis (CH_2Cl_2) ν (cm^{-1}) (ϵ , $l\ mol^{-1}\ cm^{-1}$): 15 822 (280); 22 401 (910).

3.5. Synthesis of $(C_3TAC)Cr(CH_2Ph)_3$ (**2b**)

Reaction of benzyl sodium (100 mg, 0.88 mmol) and **1b** (47 mg, 0.096 mmol) analogous to **2a** yielded 54 mg (71%) of greenish brown **2b**, m.p. 90–105°C (dec.). Anal. Calc. for $C_{42}H_{60}N_3Cr$ (658.95): C, 76.55; H, 9.18; N, 6.38%. Found: C, 76.61; H, 9.88; N, 5.87% (after addition of KNO_3). IR (KBr) ν (cm^{-1}): 408(m); 422(m); 526(m); 698(s); 729(m); 746(s); 799(m); 880(w); 893(w); 918(m); 946(s); 967(m); 986(m); 997(w); 1004(w); 1027(m); 1062(m); 1077(m); 1091(m); 1125(s); 1151(w); 1172(m); 1210(s); 1258(m); 1301(w); 1346(w); 1378(m); 1409(w); 1420(w);

Table 1
Crystallographic data and data collection for **2b**·1.5toluene

Molecular formula	$C_{52.5}H_{68}CrN_3$
Molecular weight	793.10
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal dimensions (mm)	$0.21 \times 0.21 \times 0.42$
<i>a</i> (Å)	11.761(3)
<i>b</i> (Å)	16.211(3)
<i>c</i> (Å)	23.791(4)
β (°)	97.17(2)
<i>V</i> (Å ³)	4500(2)
<i>Z</i>	4
<i>D</i> _{calc.} (g cm ⁻³)	1.171
Temperature (K)	166(2)
Radiation	Mo K α ($\lambda = 0.71069$ Å)
μ (Mo K α) (mm ⁻¹)	0.284
<i>F</i> (000)	1712
Scan type	ω -2 θ
θ -range (°)	1–22
Index ranges	$0 \leq h \leq 12, 0 \leq k \leq 17,$ $-25 \leq l \leq 25$
Total No. of reflections	6199
No. of independent reflections	3746 [$R_{int.} = 0.0168$]
[$I > 2\sigma(I)$]	
No. of parameters refined	523
$R = \sum F_o - F_c / \sum F_o $	0.049
$wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$	0.109
Goodness-of-fit on F^2	1.076
Largest diff. peak and hole (e Å ⁻³)	0.373 and -0.236

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for (C_3TAC) or $(CH_2Ph)_3 \cdot 1.5$ toluene

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Cr	2127(1)	1607(1)	6943(1)	21(1)
C(1)	567(4)	456(3)	6465(2)	25(1)
N(1)	1798(3)	297(2)	6618(1)	21(1)
C(10)	2276(3)	-220(3)	6176(2)	23(1)
C(11)	3559(4)	-372(3)	6329(2)	20(1)
C(12)	4043(4)	-841(3)	5853(2)	35(1)
C(13)	3409(4)	-1645(3)	5709(2)	36(1)
C(14)	2132(4)	-1486(3)	5566(2)	40(1)
C(15)	1655(4)	-1040(3)	6053(2)	33(1)
C(2)	1960(4)	-55(3)	7198(2)	25(1)
N(2)	1657(3)	629(2)	7560(1)	20(1)
C(20)	2065(4)	463(3)	8172(2)	23(1)
C(21)	1950(4)	1216(3)	8540(2)	33(1)
C(22)	2518(4)	1040(3)	9149(2)	37(1)
C(23)	1977(4)	307(3)	9399(2)	34(1)
C(24)	2043(4)	-448(3)	9027(2)	34(1)
C(25)	1494(4)	-279(3)	8413(2)	30(1)
C(3)	425(3)	785(3)	7435(2)	24(1)
N(3)	280(3)	1118(2)	6848(1)	21(1)
C(30)	-001(3)	1468(3)	6701(2)	28(1)
C(31)	-1865(4)	842(3)	6678(2)	40(1)
C(32)	-3035(4)	1271(4)	6577(2)	58(2)
C(33)	-3131(4)	1784(4)	6031(2)	54(2)
C(34)	-2156(4)	2382(3)	6044(2)	51(2)
C(35)	-993(4)	1957(3)	6151(2)	39(1)
C(40)	3919(4)	1482(3)	7167(2)	28(1)
C(41)	4598(3)	2123(3)	7498(2)	25(1)
C(42)	4813(4)	2087(3)	8092(2)	35(1)
C(43)	5451(4)	2680(4)	8400(2)	45(1)
C(44)	5903(4)	3338(3)	8139(2)	43(1)
C(45)	5699(4)	3394(3)	7554(2)	40(1)
C(46)	5059(4)	2798(3)	7239(2)	31(1)
C(50)	1998(4)	2730(3)	7389(2)	27(1)
C(51)	890(4)	3163(3)	7371(2)	24(1)
C(52)	564(4)	3780(3)	6969(2)	32(1)
C(53)	-443(4)	4223(3)	6972(2)	43(1)
C(54)	-1176(4)	4051(3)	7370(2)	44(1)
C(55)	-894(4)	3437(3)	7761(2)	34(1)
C(56)	118(4)	3006(3)	7760(2)	27(1)
C(60)	2210(4)	2277(3)	6181(2)	31(1)
C(61)	2415(4)	1820(3)	5664(2)	26(1)
C(62)	3528(4)	1606(3)	5567(2)	34(1)
C(63)	3739(4)	1154(3)	5097(2)	39(1)
C(64)	2848(5)	897(3)	4703(2)	45(1)
C(65)	1746(5)	1110(3)	4782(2)	43(1)
C(66)	1530(4)	1569(3)	5253(2)	35(1)
C(70)	1361(6)	10580(4)	958(3)	70(2)
C(71)	1419(4)	9655(3)	993(2)	40(1)
C(72)	1855(5)	9282(4)	1510(3)	57(2)
C(73)	1949(5)	8420(4)	1545(2)	54(2)
C(74)	1608(5)	7962(4)	1072(3)	58(2)
C(75)	1175(5)	8330(4)	570(2)	59(2)
C(76)	1100(4)	9163(4)	538(2)	51(2)
C(80)	4381(6)	-1241(4)	122(3)	72(2)
C(81)	4752(8)	-430(8)	13(5)	53(3)
C(82)	4589(5)	225(5)	407(2)	54(2)
C(83)	4230(9)	-562(10)	519(5)	63(4)
C(84)	4923(12)	1032(9)	315(6)	76(5)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths and angles in **2b**·1.5toluene (standard deviations in parentheses)

Cr–C(40)	2.118(4)	Cr–C(50)	2.121(4)
Cr–C(60)	2.126(4)	Cr–N(2)	2.275(3)
Cr–N(1)	2.278(4)	Cr–N(3)	2.297(3)
C(1)–N(1)	1.470(5)	N(1)–C(2)	1.484(5)
N(1)–C(10)	1.507(5)	C(40)–C(41)	1.476(6)
C(40)–Cr–C(50)	95.0(2)	C(40)–Cr–C(60)	96.5(2)
C(50)–Cr–C(60)	90.1(2)	N(2)–Cr–N(1)	61.60(12)
N(2)–Cr–N(3)	61.29(12)	N(1)–Cr–N(3)	61.68(12)
C(1)–N(1)–C(2)	107.8(3)	C(1)–N(1)–C(10)	111.6(3)
C(2)–N(1)–C(10)	114.8(3)	C(1)–N(1)–Cr	92.3(2)
C(2)–N(1)–Cr	92.6(2)	C(10)–N(1)–Cr	133.9(3)
C(41)–C(40)–Cr	121.4(3)	C(46)–C(41)–C(40)	122.0(4)

1447(s); 1452(s); 1463(m); 1481(s); 1493(w); 1495(w); 1498(w); 1591(s); 2802(w); 2853(s); 2929(s); 3008(m); 3063(m). UV-vis (CH_2Cl_2) ν (cm^{-1}) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 15 815 (230); 20 786 (630). Complex **2b** can be recrystallized from toluene by slow evaporation under argon as **2b**·1.5toluene. Anal. Calc. for $\text{C}_{52.5}\text{H}_{72}\text{N}_3\text{Cr}$ (797.17): C, 79.10; H, 9.10; N, 5.27%. Found: C, 78.18; H, 10.10; N, 5.45%.

3.6. Crystal structure determination of **2b**·1.5toluene

Crystal data and other details of the structure determination are collected in Table 1. The dark green crystals were selected using a modified device, similar to that of Veith and Bärninghausen [10]. The crystals were mounted on a glass fibre and transferred to an Enraf-Nonius CAD 4 four-circle diffractometer equipped with a low-temperature device. Unit cell parameters from 25 reflections in the range of $9.56^\circ \leq 2\theta \leq 24.26^\circ$ were obtained. Data were collected with ω - 2θ scans. Every 200 reflections, intensity data were monitored through the measurement of three standard reflections. All data were corrected for Lorentz and polarization effects and absorption effects (DIFABS, min./max. 0.97/1.23) [11]. Systematic absence of reflections hkl for $h+l = \text{odd}$ and $h00 = \text{odd}$ indicated the centrosymmetric space group $P2_1/n$. The structure was solved using direct methods (SHELX-86) [12] and difference-Fourier methods (SHELX-93) [13]. The molecule was refined against F_o^2 by full-matrix least-squares tech-

niques. Hydrogen atoms were placed on calculated positions with $U_{\text{iso}} = 0.08 \text{ \AA}^2$. Every $(\text{Cy}_3\text{TAC})\text{Cr}(\text{CH}_2\text{Ph})_3$ molecule crystallizes with 1.5 molecules of toluene. The toluene molecule which belongs to two assymetrical units is disordered in two positions which are connected via an inversion centre. The final values of the refined positional parameters are presented in Table 2 and the selected bond lengths and angles in Table 3. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404071 for **2b**, the names of the authors, and the journal citation.

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