

Structure of Hexakis(2,6-diisopropylphenyl isocyanide)chromium(0)

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Abstract. $[\text{Cr}(\text{C}_{13}\text{H}_{17}\text{N})_6]$, $M_r = 1175.7$, monoclinic, $P2_1/c$, $a = 12.443$ (5), $b = 12.927$ (7), $c = 23.302$ (8) Å, $\beta = 104.03$ (3)°, $V = 3636$ (3) Å³, $Z = 2$, $D_x = 1.07$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.54178$ Å, $\mu = 1.617$ mm⁻¹, $F(000) = 1272$, $T = 209$ K, $R = 0.0848$ for 3239 unique observed [$F \geq 3\sigma(F)$] reflections and 385 parameters. The Cr atom is sitting on a center of inversion and has an octahedral coordination sphere with Cr—C distances of 1.917 (5), 1.924 (6) and 1.927 (5) Å. The C—Cr—C bond angles range from 88.5 (2) to 92.0 (2)°. C—N≡C—Cr—C≡N—C displays an S-shape distortion about the Cr metal center, with C—N≡C angles of 163.7 (5), 168.4 (5), and 168.0 (5)° and Cr—C≡N angles of 176.9 (5), 177.5 (5) and 176.8 (5)°.

Introduction. Recently we have reported the electron transfer kinetics of Cr⁰, Cr^I and Cr^{II} hexakis(2,6-diisopropylphenyl isocyanides) (CNdipp) (Anderson & Wherland, 1989, 1990, 1991). We have measured the self-exchange rate constants for $\text{Cr}(\text{CNdipp})_6^{0/+1}$ and $\text{Cr}(\text{CNdipp})_6^{+1/+2}$ as a function of concentration, temperature, solvent and added electrolyte. We have also studied cross reactions of the reduction of the Cr^{II} with a series of Co^{II} clathrochelates as a function of concentration, temperature, pressure and added electrolyte. We became interested in the Cr complexes because they are substitution inert in three oxidation states and are soluble and stable in non-aqueous solvents over a large temperature range. As an important part of these studies we have completed the structural characterization of the Cr⁰ complex.

Experimental. The ligand 2,6-diisopropylphenyl isocyanide (CNdipp) was prepared from the corresponding aniline (Aldrich) utilizing dichlorocarbene generated by a phase-transfer method (Weber & Gokel, 1977). The hexakis(2,6-diisopropylphenyl isocyanide)chromium(0) was synthesized from $\text{Cr}_2(\text{CH}_3\text{CO})_4(\text{H}_2\text{O})$ by a standard method (Essenmacher & Treichel, 1977). The chromium acetate, isocyanide and dry ethanol were kept under nitrogen during the entire process. The reaction mixture was stirred for 20–40 min, after which red crystals of

$\text{Cr}(\text{CNdipp})_6$ precipitated. The complex has been characterized by elemental analysis and ¹H NMR, IR and visible spectroscopy (Anderson & Wherland, 1989). Crystals of $\text{Cr}(\text{CNdipp})_6$ were grown from a solution of methylene chloride and hexanes (70/30). The solution was allowed to evaporate for 1–3 h in a nitrogen atmosphere. One of the air and moisture sensitive crystals was mounted on a glass fiber and coated with an amorphous resin to prevent deterioration on long exposure to air.

A hexagonally shaped, bright red crystal with dimensions of 0.3 × 0.4 × 0.5 mm was selected for data collection on a Nicolet R3m diffractometer with a graphite monochromator (Campana, Shepard & Litchman, 1981). A Nicolet LT2 low-temperature device was used to collect the data at 209 K. Lattice constants from 25 reflections in the range $41 < 2\theta < 45^\circ$. Data were collected with ω scans (2°); two check reflections monitored every 96 reflections (01 $\bar{3}$ and 222) showed no systematic excursions; 5096 total reflections out to $2\theta = 110^\circ$, 4552 unique reflections with $R(\text{merge}) = 0.0240$; hkl ranges, $0 \leq h \leq 11$, $0 \leq k \leq 11$, $-20 \leq l \leq 20$. Empirical ψ -scan absorption corrections were applied (SHELXTL program XEMP; Sheldrick, 1985) assuming an ellipsoidally shaped crystal ($0.526 < T < 0.901$).

The structure solution was obtained via the direct methods routine SOLV in the SHELXTL 5.1 crystallographic program package and the refinements also used that set of programs (Sheldrick, 1985). A difference synthesis based on the Cr and N positions obtained from SOLV yielded the C-atom positions. H atoms on the isopropyl groups were constrained to ideal locations (C—H = 0.96 Å) and assigned isotropic thermal parameters 1.2 times larger than the associated C atoms; H atoms on the rings were assigned isotropic thermal parameters fixed at 0.08 Å².

The final refinement resulted in $R = 0.0848$ (3σ data set) and 0.1137 (all data) and $wR = 0.0917$ (3σ data set) and 0.0917 (all data), where $w = 1/[\sigma^2(F) + g(F)^2]$, with $g = 0.00249$. The goodness of fit was 1.505, with parameter changes in the final cycle of least squares of $|\Delta/\sigma|_{\text{max}} = 0.02$. The largest peak on the final difference map was 0.5 e Å⁻³ near Cr, while

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (\AA^2) for Cr(CNdipp)₆

	x	y	z	U_{eq}^*
Cr	0	0	0	41 (1)
N(1)	1884 (4)	1231 (3)	813 (2)	56 (2)
N(2)	1657 (4)	-1795 (4)	101 (2)	58 (2)
N(3)	-886 (4)	-732 (4)	1062 (2)	62 (2)
C(1)	1158 (4)	791 (4)	512 (2)	47 (2)
C(2)	1017 (4)	-1133 (4)	69 (2)	46 (2)
C(3)	-524 (4)	-474 (4)	666 (2)	47 (2)
C(4)	2500 (3)	2994 (3)	875 (1)	61 (2)
C(5)	3308	3731	1107	72 (3)
C(6)	4280	3435	1511	85 (3)
C(7)	4446	2402	1683	74 (3)
C(8)	3638	1665	1451	62 (2)
C(9)	2665	1961	1047	54 (2)
C(10)	1388 (5)	3313 (5)	440 (3)	77 (3)
C(11)	495 (5)	3412 (6)	776 (3)	92 (3)
C(12)	1490 (7)	4290 (5)	96 (4)	101 (4)
C(13)	3830 (6)	489 (5)	1613 (3)	87 (3)
C(14)	4249 (7)	-63 (6)	1133 (4)	115 (4)
C(15)	4587 (10)	333 (8)	2213 (4)	177 (6)
C(16)	-929 (4)	-156 (3)	2031 (2)	88 (3)
C(17)	-1390	-220	2519	120 (4)
C(18)	-2217	-945	2527	121 (5)
C(19)	-2584	-1606	2046	112 (4)
C(20)	-2123	-1542	1558	82 (3)
C(21)	-1295	-817	1550	64 (2)
C(28)	2976 (4)	-2921 (3)	-174 (2)	76 (3)
C(29)	3854	-3618	-17	106 (4)
C(30)	4245	-3914	573	121 (5)
C(31)	3757	-3514	1005	99 (4)
C(32)	2878	-2817	847	71 (3)
C(33)	2488	-2521	258	64 (2)
C(34)	2567 (7)	-2559 (6)	-829 (3)	102 (4)
C(37)	2247 (6)	-2400 (5)	1304 (3)	89 (3)
C(22)	-23 (8)	717 (8)	1995 (4)	137 (5)
C(23)	-98 (10)	1662 (7)	2311 (5)	176 (7)
C(24)	1073 (8)	178 (8)	2179 (5)	149 (6)
C(25)	-2531 (7)	-2285 (6)	1010 (3)	111 (4)
C(26)	-2877 (9)	-3324 (7)	1200 (5)	161 (6)
C(35)	2602 (10)	-3405 (7)	-1283 (4)	158 (6)
C(36)	3223 (8)	-1627 (6)	-912 (4)	124 (5)
C(38)	2933 (9)	-2459 (7)	1949 (3)	142 (5)
C(39)	1129 (6)	-2916 (6)	1214 (3)	92 (3)
C(27)	-3383 (7)	-1746 (8)	550 (4)	128 (5)

* The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

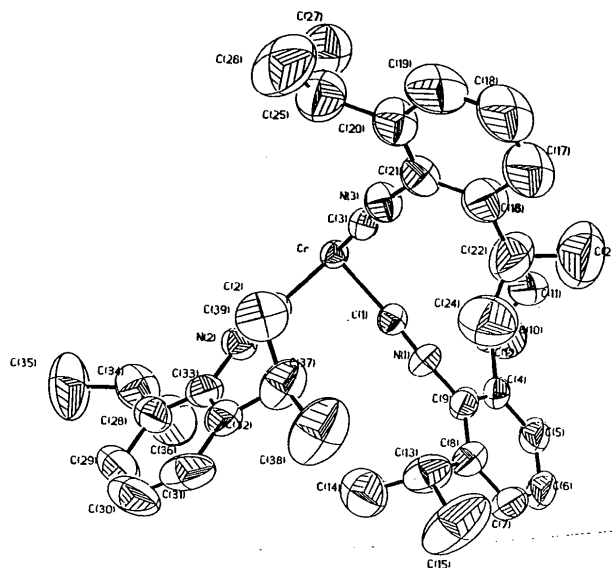
the most negative excursion was -0.5 e \AA^{-3} . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Extinction corrections were made. Atomic coordinates are listed in Table 1 and bond distances and angles are given in Table 2. A view of the structure is shown in Fig. 1.*

Discussion. The temperature was chosen because Cr(CNdipp)₆ had a phase transition at approximately 198 K. From initial studies this phase transition is irreversible. The average metal-carbon distance for the Cr⁰ complex (1.922 Å) is slightly shorter than that found for the Cr(CNC₆H₅)₆ complex (1.938 Å) (Ljungstrom, 1978). The shortening of the chromium coordinated carbon bond distances upon changing from the smaller, less sterically

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53874 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°) for Cr(CNdipp)₆

Cr—C(1)	1.927 (5)	C(13)—C(8)	1.571 (8)
Cr—C(2)	1.917 (5)	C(13)—C(14)	1.522 (12)
Cr—C(3)	1.924 (6)	C(13)—C(15)	1.497 (11)
Cr—C(1A)	1.927 (5)	C(34)—C(28)	1.558 (8)
Cr—C(2A)	1.917 (5)	C(34)—C(35)	1.529 (13)
Cr—C(3A)	1.924 (6)	C(34)—C(36)	1.495 (12)
N(1)—C(1)	1.150 (6)	C(37)—C(32)	1.564 (9)
N(1)—C(9)	1.370 (5)	C(37)—C(38)	1.540 (9)
N(2)—C(2)	1.159 (7)	C(37)—C(39)	1.511 (10)
N(2)—C(33)	1.378 (6)	C(22)—C(16)	1.612 (11)
N(3)—C(3)	1.169 (8)	C(22)—C(23)	1.441 (15)
N(3)—C(21)	1.358 (7)	C(22)—C(24)	1.498 (14)
C(10)—C(4)	1.560 (7)	C(25)—C(20)	1.579 (9)
C(10)—C(11)	1.513 (11)	C(25)—C(26)	1.509 (13)
C(10)—C(12)	1.517 (10)	C(25)—C(27)	1.487 (11)
C(1)—Cr—C(2)	88.5 (2)	C(5)—C(4)—C(10)	120.9 (3)
C(1)—Cr—C(3)	91.0 (2)	C(9)—C(4)—C(10)	119.1 (3)
C(2)—Cr—C(3)	92.0 (2)	C(7)—C(8)—C(13)	121.0 (3)
C(1)—Cr—C(1A)	180.0 (1)	C(9)—C(8)—C(13)	119.0 (3)
C(2)—Cr—C(1A)	91.5 (2)	N(1)—C(9)—C(4)	120.3 (2)
C(3)—Cr—C(1A)	89.0 (2)	N(1)—C(9)—C(8)	119.7 (2)
C(1)—Cr—C(2A)	91.5 (2)	C(4)—C(10)—C(11)	109.4 (5)
C(2)—Cr—C(2A)	180.0 (1)	C(4)—C(10)—C(12)	112.9 (5)
C(3)—Cr—C(2A)	88.0 (2)	C(11)—C(10)—C(12)	111.7 (6)
C(1A)—Cr—C(2A)	88.5 (2)	C(8)—C(13)—C(14)	109.7 (5)
C(1)—Cr—C(3A)	89.0 (2)	C(8)—C(13)—C(15)	112.3 (6)
C(2)—Cr—C(3A)	88.0 (2)	C(14)—C(13)—C(15)	111.8 (7)
C(3)—Cr—C(3A)	180.0 (1)	C(17)—C(16)—C(22)	121.0 (4)
C(1A)—Cr—C(3A)	91.0 (2)	C(21)—C(16)—C(22)	118.9 (4)
C(2A)—Cr—C(3A)	92.0 (2)	C(19)—C(20)—C(25)	120.5 (4)
C(1)—N(1)—C(9)	163.7 (5)	C(21)—C(20)—C(25)	119.5 (4)
C(2)—N(2)—C(33)	168.4 (5)	N(3)—C(21)—C(16)	120.5 (3)
C(3)—N(3)—C(21)	168.0 (5)	N(3)—C(21)—C(20)	119.5 (3)
Cr—C(1)—N(1)	176.9 (5)	C(29)—C(28)—C(34)	120.0 (4)
Cr—C(2)—N(2)	177.5 (5)	C(33)—C(28)—C(34)	119.9 (4)
Cr—C(3)—N(3)	176.8 (5)	C(31)—C(32)—C(37)	122.3 (3)

Fig. 1. Illustration of the structure of Cr(CNdipp)₆.

hindered phenyl isocyanide to the larger more sterically hindered 2,6-diisopropylphenyl isocyanide is indicative of an electronic effect. This may be partially due to a decreased amount of back bonding in the Cr(CNdipp)₆ complex. The average C≡N and N—C_{ring} distances of 1.159 (5) and 1.368 (6) Å show

no systematic variation with ligand and are in normal ranges found in other phenyl isocyanide complexes (Bohling & Mann, 1984).

The C—N≡C—Cr—C≡N—C moieties show significant angular distortion. The *trans* ligands deviate in opposite directions producing an S-type distortion. The normal 90° C—Cr—C angles range from a high value of 92.0 (2) to a low value of 88.0 (2)°. The Cr—C—N angles, normally 180°, ranged from 176.8 (5) to 177.5 (5)°. The C≡N—C angles, normally 180°, ranged from 163.7 (5) to 168.0 (5)°. In the Cr(CNC₆H₅)₆ compound the *trans* C≡N—C bonds were distorted in the same direction, producing a bowed geometry, with Cr—C 1.938 (3) Å, C≡N 1.176 (4) Å, C—Cr—C 85.9 (2)°, C≡N—C 172.9 (3)° and Cr—C≡N 173.7 (2)° (Ljungström, 1978). This same bowed geometry was observed for the Cr^I, Cr^{II} and Cr^{III} Cr(CNC₆H₅)₆ complexes and the extent of the bowing was found to increase with the oxidation state (Bohling & Mann 1984).

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Complexes of Lithium and Sodium with *sym*-(Dibenzo-14-crown-4)methylphenyl Phosphinic Acid

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Abstract. (1) (6-Methylphenylphosphinato-2,3,9,10-dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene)-lithium-ethanol (1/1), [Li(C₂₅H₂₆PO₆)]·C₂H₅OH, *M_r* = 506.46, triclinic, *P* $\bar{1}$, *a* = 10.158 (1), *b* = 10.663 (1), *c* = 12.766 (2) Å, α = 100.93 (1), β = 109.55 (1), γ = 99.10 (1)°, *V* = 1242.2 (6) Å³, *Z* = 2, *D_x* = 1.35 g cm⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 1.49 cm⁻¹, *F*(000) = 536, *T* = 295 K, *R*(*F*) = 0.048 for 1712 reflections [*I* > σ (*I*)]. (2) (6-Methylphenylphosphinato-2,3,9,10-dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene)diaquasodium trihydrate, [Na(C₂₅H₂₆PO₆)(H₂O)₂]·3H₂O, *M_r* = 566.52, triclinic, *P* $\bar{1}$, *a* = 10.493 (6), *b* = 11.770 (5), *c* = 13.162 (5) Å, α = 98.16 (3), β = 108.73 (4), γ = 108.81 (4)°, *V* = 1402 (3) Å³, *Z* = 2, *D_x* = 1.35, *D_m* = 1.34 g cm⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 1.63 cm⁻¹, *F*(000) = 600, *T* = 296 K, *R*(*F*) = 0.058 for 2849 reflections [*I* > σ (*I*)]. In neither compound is there intramolecular bonding of the phosphinate anion to the cation enclosed in the crown. Compound (1) crystallizes as dimers in which the phosphinate group of one ligand is bonded to the Li⁺ ion enclosed in the ether cavity of its partner and *vice versa*. Molecules of compound

(2) are isolated from each other by channels of water molecules.

Introduction. The crown ethers with pendant sidearms containing functional groups (lariats) are primarily of two types: the oxa crowns in which the sidearm is attached to a C atom (C pivot) and the aza or oxa-aza crowns that are of the N-pivot type. In the latter the functionality is in a position axial (*A*) to the crown by virtue of the N-bonding geometry and usually coordinates any cation enclosed in the crown (Gandour, Fronczek, Gatto, Minganti, Schultz, White, Arnold, Mazzocchi, Miller & Gokel, 1986; Arnold, Echevoyen, Fronczek, Gandour, Gatto, White & Gokel, 1987). For C-pivot crowns the sidearm may be *A* or *E* (equatorial) (Echevoyen, Kaifer, Durst, Schultz, Dishong, Goli & Gokel, 1984). In one case, a substituted 18-crown-6 derived from tartaric acid, two carboxylate groups occupy *A* positions but they are induced to be there by bulky vicinal substituents (Behr, Lehn, Moras & Thierry, 1981).