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Trichloro(1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane-*N*,*N'*,*N''*)chromium

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Abstract

The facially coordinated macrocyclic ligand 1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane (''Bu$_3$tacn) plus three Cl ligands assume a distorted octahedral geometry around the Cr atom in the title compound, [CrCl$_3$(C$_{18}$H$_{39}$N$_3$)]. The average Cr—N distance of 2.149 (5) Å is slightly longer than the distance of 2.090 (8) Å found in *fac*-(diethylenetriamine)CrCl$_3$ [Fowlie, House, Robinson & Rumball (1970). *J. Chem. Soc. A*, pp. 803–806] and that of 2.089 (4) Å found in [(Me$_3$tacn)$_2$Cr$_2$(OH)$_3$]I$_3$ [Wieghardt, Chaudhuri, Nuber & Weiss (1982). *Inorg. Chem.* **21**, 3086–3090], indicating some repulsion between ''Bu$_3$tacn and the Cl atoms. The Cr—Cl distances average 2.324 (5) Å.

Comment

An important method for controlling the course of olefin chain-growth reactions involves ligand-based

catalyst design. In particular, transition metal catalyst activities can be tuned by complexation of the metals with various multidentate ligands. Commercially significant procedures based on such an approach include metallocene-catalyzed polyolefin production (Kaminsky, Engehausen, Zoumis, Spaleck & Rohrmann, 1992) and the Ni-catalyzed olefin chain-growth process (Keim, 1990).

Our efforts to develop new Cr-based ethylene oligomerization catalysts led to the synthesis of trichloro(1,4,7-tri-*n*-butyl-1,4,7-triazacyclononane)-chromium, (''Bu$_3$tacn)CrCl$_3$ (1). This new complex was made by procedures analogous to those reported for the preparation of the 1,4,7-triisopropyl derivative, ('Pr$_3$tacn)CrCl$_3$, which has been characterized by spectroscopic means only (Haselhorst, Stoetzel, Strassburger, Walz, Wieghardt & Nuber, 1993).

(1)
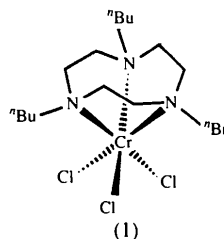
The ability of 1,4,7-triazacyclononane and its derivatives to form stable complexes with a wide variety of metals is well known (Chaudhuri & Wieghardt, 1987). These ligands proved to be superior for our Cr-based ethylene oligomerization/trimerization catalysts because variation of the alkyl groups bound to the N atoms allowed selection between two reaction pathways. Smaller groups, like methyl, gave catalysts favoring oligomerization, while larger groups, like butyl, gave catalysts favoring trimerization to hexene.

An *ORTEP* (Johnson, 1965) drawing of (1) is shown in Fig. 1. The macrocyclic ligand coordinates facially. The distance between Cr and the ring centroid (defined by the three N atoms) is 1.395 Å. The ligand plus three Cl atoms assume a distorted octahedral geometry around the Cr atom. The molecule possesses approximate C_3 symmetry along the Cr–ring-centroid axis. The average of the three N—Cr—N bite angles is 82.4 (3) , a deviation of 7.6 (3) from an ideal octahedral value. By comparison, in the closely related complex *fac*-(diethylenetriamine)CrCl$_3$ (Fowlie, House, Robinson & Rumball, 1970), the three N—Cr—N angles are 89.7 (6) for the unconnected pair of N atoms and 82.8 (6) and 83.7 (5) for the connected pairs. The average Cr—N distance of 2.149 (5) Å is slightly longer than the value of 2.090 (8) Å found in *fac*-(diethylenetriamine)CrCl$_3$ (Fowlie, House, Robinson & Rumball, 1970) and that of 2.089 (4) Å in

[(Me₃tacn)₂Cr₂(OH)₃]I₃ (Wieghardt, Chaudhuri, Nuber & Weiss, 1982), indicating some repulsion between "Bu₃tacn and the Cl atoms. The ring conformation of "Bu₃tacn is normal for an (R_3tacn)metal complex.

Noteworthy with regard to catalytic activity is the metal–ligand cone angle. Cone angles were calculated using the method of Tolman (1977). Those of the (N1,N2,N3) and (C7,C11,C15) rings to Cr are 158.4 and 222.2 , respectively. By comparison, the cone angle of Cp*—Cr is 169.3 for [Cp*Cr(py)₂Et]PF₆ (Thomas, Noh, Schulte, Sendlinger & Theopold, 1991). Access to the Cr atom of (1) is clearly limited by the sterically demanding triazacyclononane ring.
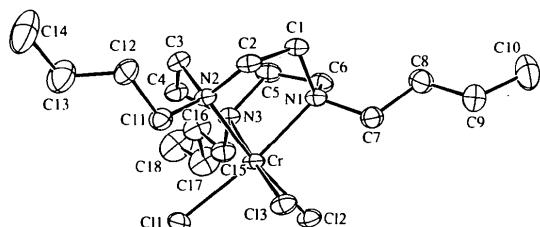

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound, with ellipsoids drawn at the 30% probability level. H atoms are omitted for clarity.

Experimental

Crystal data

[CrCl₃(C₁₈H₃₉N₃)]
$M_r = 455.9$
Monoclinic
$P2_1/c$
$a = 13.5320\ (7)$ Å
$b = 13.817\ (1)$ Å
$c = 14.0625\ (9)$ Å
$\beta = 117.906\ (6)°$
$V = 2323.6\ (6)$ Å³
$Z = 4$
$D_x = 1.303$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 0.84$ mm⁻¹
$T = 297$ K
Prism fragment
$0.30 \times 0.20 \times 0.15$ mm
Emerald green
Crystal source: evaporation from methanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{min} = 0.935$, $T_{max} = 0.999$
4453 measured reflections
4084 independent reflections
2939 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -16 \rightarrow 14$
3 standard reflections frequency: 167 min intensity variation: <2%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.035$
$S = 1.475$
2939 reflections
383 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.41$ e Å⁻³
$\Delta\rho_{min} = -0.08$ e Å⁻³
Extinction correction:
$1/(I + gI_c)$ applied to F_c
Extinction coefficient:
$g = 3.5\ (13) \times 10^{-8}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cr	0.10869 (3)	0.25725 (3)	0.78101 (3)	2.754 (8)
Cl1	0.26906 (6)	0.21931 (5)	0.93859 (5)	4.07 (2)
Cl2	0.06002 (5)	0.38213 (5)	0.86127 (5)	3.69 (1)
Cl3	0.00250 (5)	0.14573 (5)	0.81868 (5)	3.82 (1)
N1	−0.0266 (2)	0.2946 (2)	0.6262 (1)	2.94 (5)
N2	0.1453 (2)	0.1545 (2)	0.6878 (1)	2.90 (5)
N3	0.1995 (2)	0.3537 (2)	0.7297 (1)	3.19 (5)
C1	−0.0288 (2)	0.2238 (2)	0.5441 (2)	3.29 (6)
C2	0.0330 (2)	0.1322 (2)	0.5968 (2)	3.27 (6)
C3	0.2195 (2)	0.2017 (2)	0.6487 (2)	3.53 (6)
C4	0.2791 (2)	0.2884 (2)	0.7158 (2)	3.73 (6)
C5	0.1206 (2)	0.3990 (2)	0.6244 (2)	3.85 (7)
C6	0.0018 (2)	0.3938 (2)	0.6045 (2)	3.63 (7)
C7	−0.1391 (2)	0.2958 (2)	0.6231 (2)	3.79 (7)
C8	−0.2319 (2)	0.3473 (2)	0.5292 (2)	4.69 (8)
C9	−0.3439 (2)	0.3264 (3)	0.5227 (3)	6.0 (1)
C10	−0.4384 (3)	0.3892 (4)	0.4463 (3)	9.1 (1)
C11	0.1988 (2)	0.0625 (2)	0.7455 (2)	3.82 (6)
C12	0.2173 (2)	−0.0152 (2)	0.6782 (2)	4.23 (7)
C13	0.3381 (3)	−0.0482 (3)	0.7267 (3)	6.7 (1)
C14	0.3545 (3)	−0.1311 (3)	0.6661 (4)	9.2 (1)
C15	0.2609 (2)	0.4318 (2)	0.8107 (2)	4.13 (7)
C16	0.3461 (2)	0.4894 (2)	0.7941 (2)	5.27 (8)
C17	0.3834 (3)	0.5775 (3)	0.8670 (3)	6.7 (1)
C18	0.4778 (3)	0.6327 (3)	0.8664 (3)	8.6 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cr—Cl1	2.3223 (6)	N3—C15	1.505 (3)
Cr—Cl2	2.3196 (9)	C1—C2	1.507 (3)
Cr—Cl3	2.3308 (9)	C3—C4	1.504 (4)
Cr—N1	2.151 (2)	C5—C6	1.498 (4)
Cr—N2	2.142 (2)	C7—C8	1.509 (3)
Cr—N3	2.154 (2)	C8—C9	1.503 (5)
N1—C1	1.502 (3)	C9—C10	1.502 (5)
N1—C6	1.494 (3)	C11—C12	1.526 (4)
N1—C7	1.503 (4)	C12—C13	1.517 (4)
N2—C2	1.491 (3)	C13—C14	1.505 (7)
N2—C3	1.502 (4)	C15—C16	1.506 (5)
N2—C11	1.500 (3)	C16—C17	1.518 (5)
N3—C4	1.486 (4)	C17—C18	1.491 (6)
N3—C5	1.499 (3)		
Cl1—Cr—Cl2	93.15 (3)	C3—N2—C11	109.3 (2)
Cl1—Cr—Cl3	91.95 (3)	C4—N3—C5	110.4 (2)
Cl1—Cr—N1	172.96 (7)	C4—N3—C15	110.9 (2)
Cl1—Cr—N2	93.08 (5)	C5—N3—C15	109.6 (2)
Cl1—Cr—N3	91.97 (5)	N1—C1—C2	111.2 (2)
Cl2—Cr—Cl3	92.03 (3)	N2—C2—C1	110.9 (2)
Cl2—Cr—N1	90.76 (6)	N2—C3—C4	111.7 (2)
Cl2—Cr—N2	172.13 (6)	N3—C4—C3	110.9 (2)
Cl2—Cr—N3	92.25 (7)	N3—C5—C6	111.8 (2)
Cl3—Cr—N1	93.75 (6)	N1—C6—C5	111.2 (2)
Cl3—Cr—N2	92.55 (6)	N1—C7—C8	116.6 (3)

Cl3—Cr—N3	174.02 (5)	C7—C8—C9	111.4 (3)
N1—Cr—N2	82.56 (7)	C8—C9—C10	115.4 (3)
N1—Cr—N3	82.02 (7)	N2—C11—C12	116.0 (2)
N2—Cr—N3	82.74 (9)	C11—C12—C13	112.8 (2)
C1—N1—C6	110.8 (2)	C12—C13—C14	112.8 (3)
C1—N1—C7	109.2 (2)	N3—C15—C16	116.9 (3)
C6—N1—C7	109.8 (2)	C15—C16—C17	110.8 (3)
C2—N2—C3	111.3 (2)	C16—C17—C18	114.9 (4)
C2—N2—C11	109.2 (2)		
C6—N1—C1—C2	134.1 (2)	C4—N3—C5—C6	133.3 (2)
C7—N1—C1—C2	−104.8 (3)	C15—N3—C5—C6	−104.2 (3)
C1—N1—C6—C5	−68.5 (3)	C4—N3—C15—C16	51.7 (3)
C7—N1—C6—C5	170.8 (2)	C5—N3—C15—C16	−70.4 (3)
C1—N1—C7—C8	−74.8 (3)	N1—C1—C2—N2	−49.2 (3)
C6—N1—C7—C8	46.9 (3)	N2—C3—C4—N3	−49.2 (3)
C3—N2—C2—C1	−65.4 (3)	N3—C5—C6—N1	−47.4 (3)
C11—N2—C2—C1	173.9 (2)	N1—C7—C8—C9	168.3 (3)
C2—N2—C3—C4	133.9 (2)	C7—C8—C9—C10	168.3 (3)
C11—N2—C3—C4	−105.3 (2)	N2—C11—C12—C13	124.9 (3)
C2—N2—C11—C12	60.0 (3)	C11—C12—C13—C14	174.7 (3)
C3—N2—C11—C12	−62.0 (3)	N3—C15—C16—C17	168.4 (3)
C5—N3—C4—C3	−67.3 (3)	C15—C16—C17—C18	172.9 (3)
C15—N3—C4—C3	171.0 (2)		

Isotropic displacement parameters for the ring H atoms range 2.4 (5)–4.2 (6) Å^2 and the C—H distances range 0.89 (2)–0.99 (2) Å. The H atoms of the butyl groups have B values in the range 2.9 (5)–19 (2) Å^2 and C—H distances in the range 0.86 (2)–1.08 (4) Å. Programs used include the Enraf–Nonius SDP system (Frenz, 1978) and ORTEP (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-trans-[{N3P3Cl4(C6H5)(PPh2)}Mn-(CO)2(bipy){P(OPh)3}]PF6. A Cationic Manganese–Carbonyl Complex with a Phosphazenylphosphine Ligand

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Abstract

The structure of cis-trans-(bipyridine-N,N')dicarbonyl-[diphenyl(2-phenyl-4,4,6,6-tetrachloro-2-cyclotriphos-phazenyl)phosphine-P](triphenyl phosphite-P)mangan-ese(I) hexafluorophosphate, $[Mn(C_{18}H_{15}O_3P)(C_{10}H_8-N_2)(C_{18}H_{15}Cl_4N_3P_4)(CO)_2]PF_6$, consists of discrete complex cations and PF_6^- anions linked by several weak C—H$\cdots$O and C—H$\cdots$F interactions. The cation is a very distorted octahedral manganese–dicarbonyl fragment having cis-trans stereochemistry and bearing triphenylphosphite, bipyridine and phosphazenylphosphine $[N_3P_3Cl_4(Ph)(PPh_2)]$ ligands. Analysis of the structure of the complex reveals that the coordination of the phosphazenylphosphine ligand to the cationic manganese–carbonyl fragment induces only minor changes in the phosphazene ring, affecting only the P5—P3 bond length.

Comment

The presence of phosphine in a phosphazene ring molecule, attached either directly to the ring P atoms or indirectly via pendant groups, is of interest because the resulting ligands and their complexes may be useful as models for high polymeric analogues (Allcock, Manners, Mang & Parvaez, 1990). The phosphazenylphosphine ligand $N_3P_3Cl_4(C_6H_5)(PPh_2)$ has been coordinated previously to a neutral $Cr(CO)_5$ fragment and the X-ray structure determination of the resulting complex showed that no significant changes took place in the structure of the phosphazene ring upon coordination of the metal to the ligating PPh_2 group (Allcock, Manners, Mang & Parvaez, 1990). In order to determine the effect of a similar oc-