metal-organic papers

Trichloro(perdeuteroacetonitrile)bis(triphenylphosphine)rhodium(III)

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The title complex, [RhCl$_3$(PPh$_3$)$_2$(NCCD$_3$)], crystallizes with two independent, but essentially identical, molecules in the asymmetric unit. Rh is octahedrally coordinated by three *mer*-chloro ligands, two mutually *trans*-phosphines, and a molecule of the NMR solvent perdeuteroacetonitrile.

Key indicators

Single-crystal X-ray study
$T = 160$ K
Mean σ(C–C) = 0.009 Å
R factor = 0.053
wR factor = 0.121
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), was obtained as a minor product during a study of diboration reactions catalysed by metal complexes. It consists of a discrete neutral mononuclear complex of Rh^{III}, with two independent molecules in the asymmetric unit (Figs. 1 and 2). There are no special inter-molecular interactions.

(I)
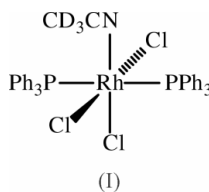
Two triphenylphosphine ligands lie *trans* to each other, and the other four coordination sites are occupied by three *mer*-chloro ligands and one molecule of the perdeuteroacetonitrile solvent used for NMR purposes. The solvent molecule lies opposite the longest Rh—Cl bond in each of the two independent molecules of the complex, for which the molecular structure is essentially identical. Deviations from ideal octahedral geometry are minor. Bond lengths are within expected ranges. The coordinated perdeuteroacetonitrile ligands are essentially linear at both the C and N atoms of the cyano group.

Experimental

A solution of [RhCl(PPh$_3$)$_3$] (Wilkinson's catalyst; 0.018 g, 0.019 mmol) in CH$_2$Cl$_2$ (2 ml) was added with stirring to a suspension of B$_2$(O$_2$C$_6$Cl$_4$)$_2$ (0.011 g, 0.021 mmol) in CH$_2$Cl$_2$ (2 ml). On cooling to 243 K, [RhCl(PPh$_3$)$_2${B(O$_2$C$_6$Cl$_4$)}$_2$] was formed as a yellow solid. A solution of this product in CD$_3$CN, prepared for NMR spectro-scopy, deposited a small quantity of the crystalline title complex overnight.

Crystal data

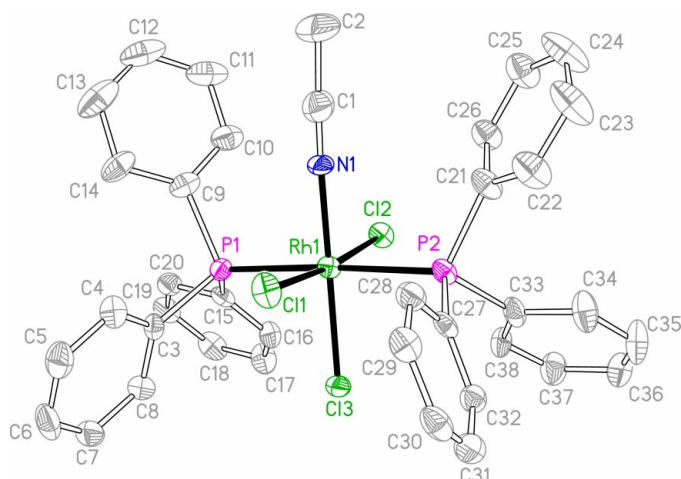|	
[RhCl$_3$(C$_{18}$H$_{15}$P)$_2$(C$_2$D$_3$N)]	$D_x = 1.505$ Mg m^{-3}
$M_r = 777.85$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 20658
$a = 26.4006$ (9) Å	reflections
$b = 14.1098$ (6) Å	$\theta = 1.8$–28.5°
$c = 19.8335$ (12) Å	$\mu = 0.85$ mm^{-1}
$\beta = 111.666$ (2)°	$T = 160$ (2) K
$V = 6866.2$ (6) Å^3	Block, orange
$Z = 8$	$0.22 \times 0.20 \times 0.16$ mm

Figure 1
The structure of one independent molecule of (I), with atom labels and 50% probability ellipsoids for non-H atoms.
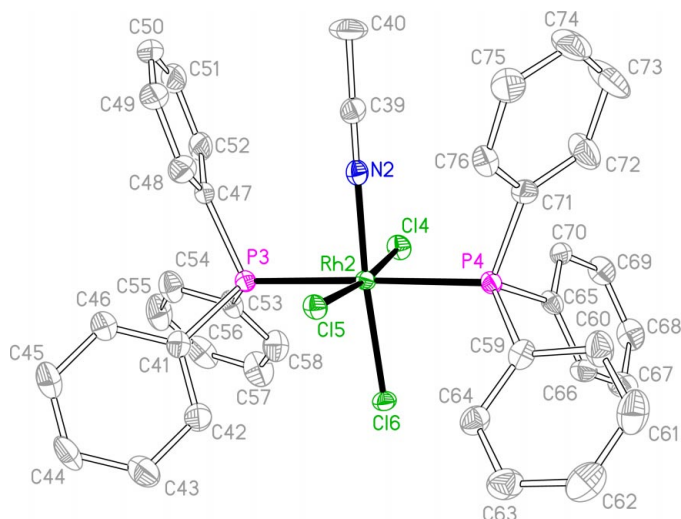

Figure 2
The structure of the other independent molecule of (I), with atom labels and 50% probability ellipsoids for non-H atoms.

Data collection

Siemens SMART CCD diffractometer	12063 independent reflections
ω rotation with narrow frames	9721 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 1997)	$R_{int} = 0.086$
	$\theta_{max} = 25.0°$
	$h = -31 \rightarrow 18$
$T_{min} = 0.83$, $T_{max} = 0.88$	$k = -16 \rightarrow 16$
35176 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 28.998P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.21$	$\Delta\rho_{max} = 0.95$ e Å^{-3}
12063 reflections	$\Delta\rho_{min} = -0.88$ e Å^{-3}
814 parameters	Extinction correction: *SHELXTL*
H-atom parameters constrained	Extinction coefficient: 0.00013 (3)

Table 1
Selected geometric parameters (Å, °).

Rh1—Cl1	2.3367 (15)	Rh2—Cl4	2.3548 (12)
Rh1—Cl2	2.3728 (14)	Rh2—Cl5	2.3867 (12)
Rh1—Cl3	2.3398 (12)	Rh2—Cl6	2.3418 (11)
Rh1—N1	2.006 (4)	Rh2—N2	1.999 (4)
Rh1—P1	2.4102 (13)	Rh2—P3	2.3843 (13)
Rh1—P2	2.3933 (13)	Rh2—P4	2.3826 (13)
Cl1—Rh1—Cl2	174.01 (5)	Cl4—Rh2—Cl5	173.32 (4)
Cl1—Rh1—Cl3	89.43 (5)	Cl4—Rh2—Cl6	89.34 (4)
Cl1—Rh1—N1	86.03 (15)	Cl4—Rh2—N2	87.93 (12)
Cl1—Rh1—P1	87.66 (5)	Cl4—Rh2—P3	87.54 (4)
Cl1—Rh1—P2	92.96 (5)	Cl4—Rh2—P4	93.73 (4)
Cl2—Rh1—Cl3	96.33 (5)	Cl5—Rh2—Cl6	95.86 (4)
Cl2—Rh1—N1	88.27 (15)	Cl5—Rh2—N2	87.14 (12)
Cl2—Rh1—P1	90.79 (5)	Cl5—Rh2—P3	88.02 (4)
Cl2—Rh1—P2	88.91 (5)	Cl5—Rh2—P4	90.81 (4)
Cl3—Rh1—N1	174.94 (15)	Cl6—Rh2—N2	175.40 (12)
Cl3—Rh1—P1	88.89 (4)	Cl6—Rh2—P3	92.98 (4)
Cl3—Rh1—P2	87.93 (5)	Cl6—Rh2—P4	86.03 (4)
N1—Rh1—P1	93.16 (13)	N2—Rh2—P3	90.59 (12)
N1—Rh1—P2	90.07 (13)	N2—Rh2—P4	90.45 (12)
P1—Rh1—P2	176.75 (5)	P3—Rh2—P4	178.39 (5)

Some data with $\theta > 25°$ were collected, but they were very weak and were not used in the refinement. H/D atoms were placed geometrically (the three D atoms of the coordinated solvent in each molecule being located from a difference map) and refined with a riding model (including free rotation about C—C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *SMART* (Siemens, 1994); cell refinement: local programs; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

References

Sheldrick, G. M. (1997). *SHELXTL.* Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1994). *SMART* and *SAINT.* Bruker AXS Inc., Madison, Wisconsin, USA.