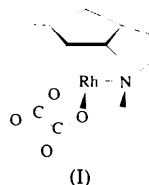


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ordination site. While for the diiodorhodium complex Cp<sup>#</sup>RhI<sub>2</sub>, the intramolecular coordination mode of the side chain was indicated by NMR data and proved by an X-ray diffraction study, only NMR data were available for the analogous oxalate compound, (I). In addition, determination of the structure of (I) is interesting because no structures of cyclopentadienyl–oxalate complexes with Group 9 elements have been reported previously.



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## Intramolecular Coordination of the Dimethylamino Group in a Rhodium–Oxalate Complex with the 1-[2-(Dimethylamino)-ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand

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### Abstract

The title compound, { $\eta^5$ -1-[2-(dimethylamino- $\kappa$ N)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}(oxalato- $\kappa^2$ O,O'')-rhodium, [Rh(C<sub>2</sub>O<sub>4</sub>)(C<sub>13</sub>H<sub>22</sub>N)], is the first rhodium–oxalate complex incorporating a cyclopentadienyl ligand. In this complex, the dimethylamino group of the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand is coordinated to the Rh atom in an intramolecular manner.

### Comment

In the course of our work with transition metal complexes of the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp<sup>#</sup>) (Jutzi & Dahlhaus, 1993), we have examined several rhodium complexes (Jutzi, Kristen, Neumann & Stammler, 1994). Complexes of this type deserve special attention because the dimethylamino group can coordinate intramolecularly to the metal centre. Thus, they can act as an intramolecular protecting group and block a vacant co-

The structure determination of (I) shows that the dimethylamino group coordinates intramolecularly to the Rh atom. The Rh–N distance of 2.188 (6) Å is in good agreement with the metal–nitrogen distances observed in isostructural complexes containing the Cp<sup>#</sup> ligand (Jutzi, Kristen, Dahlhaus, Neumann & Stammler, 1993; Jutzi, Kristen, Neumann & Stammler, 1994). In addition, the Rh atom is not exactly centred below the cyclopentadienyl ring, but is shifted towards atom C5 to a small extent. Due to the intramolecular coordination of the side chain, the methylene C10 atom is bent towards the Rh atom; the C10–C5 vector intersects the Cp<sup>#</sup> ring plane at an angle of 10.7°. The Rh–C<sub>ring</sub> distances are in the range expected for half-sandwich transition metal cyclopentadienyl complexes [2.092 (7)–2.191 (8) Å]. It

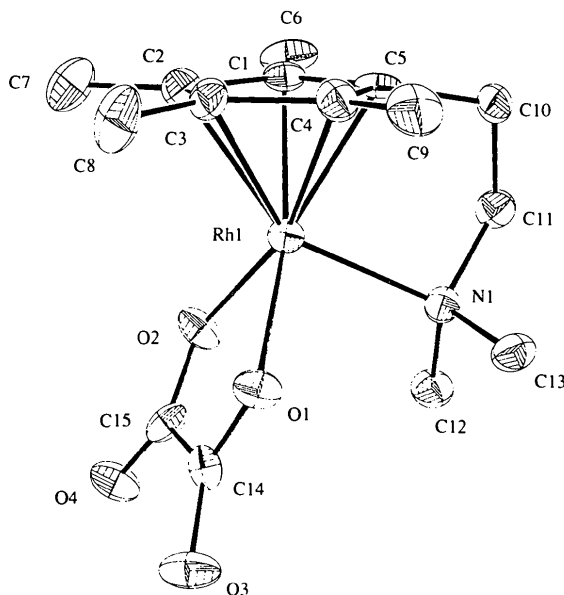


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

is difficult to say whether the intramolecular coordination influences the oxalate part of the molecule, because no cyclopentadienyl-oxalate complexes with Group 9 elements have been structurally characterized previously. However, the crystal structure of the square-planar rhodium(I) complex  $\text{NMe}_4[\text{Rh}(\text{C}_2\text{O}_4)(\text{CO})_2]$  has been reported (Real, Bayón, Lahoz & López, 1989); the bond lengths and angles of the oxalate ligand in this compound are in good agreement with those in (I). Thus, the intramolecular coordination of the dimethyl-amino group does not seem to have a decisive influence on the oxalate unit.

## Experimental

The title compound, (I), was synthesized by stirring a  $\text{CH}_2\text{Cl}_2$  solution of equal amounts of  $\text{Cp}^*\text{RhI}_2$  and silver oxalate for 6 d at room temperature with the exclusion of light. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of (I) (Jutzi, Kristen, Neumann & Stammler, 1994).

### Crystal data

$[\text{Rh}(\text{C}_2\text{O}_4)(\text{C}_{13}\text{H}_{22}\text{N})]$

$M_r = 383.25$

Monoclinic

$P2_1/n$

$a = 12.785$  (5) Å

$b = 9.265$  (4) Å

$c = 12.881$  (4) Å

$\beta = 97.39$  (3)°

$V = 1513.1$  (10) Å<sup>3</sup>

$Z = 4$

$D_x = 1.682$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 30 reflections

$\theta = 3.2$ – $9.8$ °

$\mu = 1.144$  mm<sup>-1</sup>

$T = 173$  (2) K

Needle

$0.80 \times 0.15 \times 0.05$  mm

Yellow

### Data collection

Siemens  $P2_1$  diffractometer

Wyckoff scans

Absorption correction:

$\psi$  scans (*SHELXTL-Plus*;  
Sheldrick, 1990)

$T_{\min} = 0.518$ ,  $T_{\max} =$   
0.641

3467 measured reflections

3303 independent reflections

2051 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.1007$

$\theta_{\text{max}} = 27.05$ °

$h = 0 \rightarrow 16$

$k = 0 \rightarrow 11$

$l = -16 \rightarrow 16$

3 standard reflections  
monitored every 100  
reflections

intensity decay: 1%

### Refinement

Refinement on  $F^2$

$R(F) = 0.0605$

$wR(F^2) = 0.1694$

$S = 1.126$

3280 reflections

196 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.084$

$\Delta\rho_{\text{max}} = 0.748$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.915$  e Å<sup>-3</sup>

Atomic scattering factors  
from *International Tables*  
for *Crystallography* (1992),  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Rh1	0.02727 (5)	0.10056 (7)	0.26553 (5)	0.0179 (2)
O1	-0.0297 (4)	-0.0699 (6)	0.1682 (4)	0.0236 (13)
O2	0.0583 (4)	-0.0740 (6)	0.3665 (4)	0.0251 (13)
O3	-0.0654 (5)	-0.3046 (7)	0.1722 (4)	0.0324 (14)
O4	0.0485 (5)	-0.3140 (6)	0.3734 (4)	0.0323 (14)
N1	-0.1321 (5)	0.1330 (6)	0.3061 (5)	0.0196 (14)
C1	0.1156 (6)	0.2737 (8)	0.3400 (6)	0.021 (2)
C2	0.1847 (6)	0.1879 (9)	0.2821 (6)	0.025 (2)
C3	0.1438 (6)	0.1951 (9)	0.1748 (6)	0.023 (2)
C4	0.0462 (6)	0.2777 (9)	0.1650 (6)	0.023 (2)
C5	0.0294 (7)	0.3263 (8)	0.2687 (6)	0.021 (2)
C6	0.1350 (7)	0.3048 (10)	0.4561 (6)	0.036 (2)
C7	0.2826 (6)	0.1134 (12)	0.3300 (6)	0.037 (2)
C8	0.1864 (6)	0.1210 (11)	0.0846 (6)	0.037 (2)
C9	-0.0204 (7)	0.3119 (10)	0.0616 (6)	0.033 (2)
C10	-0.0708 (6)	0.3903 (9)	0.2980 (6)	0.025 (2)
C11	-0.1268 (6)	0.2780 (9)	0.3577 (6)	0.025 (2)
C12	-0.1700 (6)	0.0261 (9)	0.3788 (6)	0.028 (2)
C13	-0.2089 (6)	0.1348 (9)	0.2099 (6)	0.026 (2)
C14	-0.0262 (6)	-0.1958 (8)	0.1211 (5)	0.018 (2)
C15	0.0336 (6)	-0.1982 (10)	0.3276 (6)	0.022 (2)

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

Rh1—O1	2.089 (5)	Rh1—C4	2.123 (8)
Rh1—C5	2.092 (7)	Rh1—C2	2.154 (8)
Rh1—C1	2.119 (8)	Rh1—N1	2.188 (6)
Rh1—O2	2.081 (5)	Rh1—C3	2.191 (8)
O1—Rh1—O2	79.1 (2)	O2—Rh1—N1	93.8 (2)
O1—Rh1—N1	89.1 (2)		

All non-H atoms were refined anisotropically. H atoms were included in calculated positions using a riding model [ $U(\text{H}) = 1.2U_{\text{eq}}$  for  $\text{CH}_2$  groups and  $U(\text{H}) = 1.5U_{\text{eq}}$  for  $\text{CH}_3$  groups]. Methyl groups were constrained to idealized symmetry with fixed C—H distances and were allowed to rotate about the C—C axes.

Data collection: *P3 Data Collection Program* (Siemens, 1989). Cell refinement: *SHELXTL-Plus* (Sheldrick, 1990). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

This work was supported by Degussa AG, BASF AG and the Fond der Chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Non-Coordination of the Dimethylamino Group in a Dinuclear Molybdenum Complex with the 1-[2-(Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand

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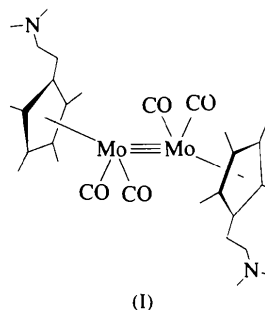
### Abstract

The title compound, tetracarbonylbis{ $\eta^5$ -1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}-dimolybdenum(*Mo—Mo*), [Mo<sub>2</sub>(C<sub>13</sub>H<sub>22</sub>N)<sub>2</sub>(CO)<sub>4</sub>], is the first molybdenum complex incorporating the hemilabile 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand. The Mo—Mo distance of 2.510(1) Å is a typical triple-bond distance. The dimethylamino group of the side chain is clearly not coordinated to the metal atom.

### Comment

Transition metal complexes incorporating the 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp<sup>#</sup>) (Jutzi & Dahlhaus, 1993) are attracting increased interest because the dimethylamino group of the side chain can coordinate to the central metal in an intramolecular manner. Various examples of these complexes have been published (Jutzi, Dahlhaus & Kristen, 1993; Jutzi, Kristen, Dahlhaus, Neumann & Stammler, 1993; Jutzi, Kristen, Neumann & Stammler, 1994). In all these cases, only complexes with an intramolecularly coordinated dimethylamino group have been structurally characterized. The structure of the title compound, (I), represents the first example of a structure having an uncoordinated side chain. The structural

information is therefore valuable as it allows correlation of a set of NMR data with this type of structure. Thus, in future, comments about the coordination mode of the dimethylamino group can be made on the basis of NMR data with higher reliability.



The title molecule consists of two symmetrical halves, each containing a Cp<sup>#</sup>Mo unit and two carbonyl groups. The side chains do not coordinate to the central metal atoms and lie on opposite sides of the Mo—Mo axis. The existence of an Mo≡Mo triple bond is inferred from the bond length of 2.510(1) Å, compared with the Mo—Mo single-bond length in [CpMo(CO)<sub>3</sub>]<sub>2</sub> of 3.235(1) Å (Adams, Collins & Cotton, 1974) and the Mo≡Mo triple-bond length in [CpMo(CO)<sub>2</sub>]<sub>2</sub> of 2.448(1) Å (Klinger, Butler & Curtis, 1975). All other

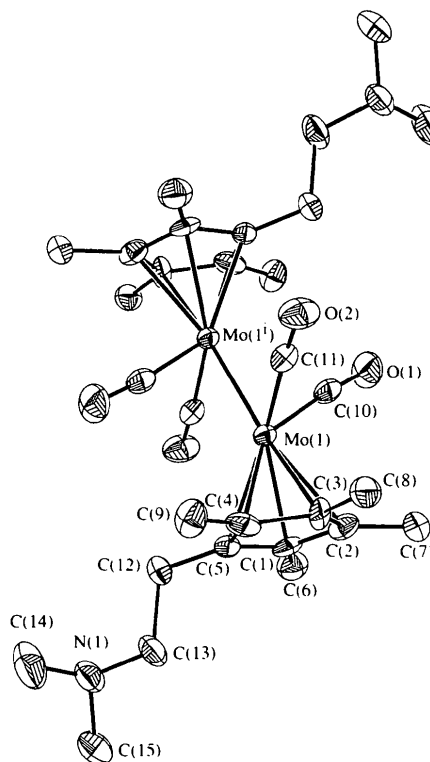


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.