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# Synthesis and molecular structure of Cr(salen)($\mu$-N)RhCl(COD): the first example of a heterobimetallic nitride-bridged complex containing chromium

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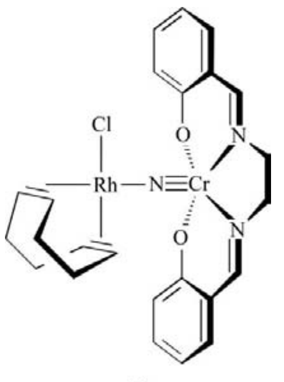
Five-coordinate Cr(N)(salen) {salen is 2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolate} reacts with $[RhCl(COD)]_2$ (COD is 1,5-cyclooctadiene) to yield the heterobimetallic nitride-bridged title compound, namely chlorido-2$\kappa$*Cl*-[2($\eta^4$)-1,5-cyclooctadiene]{2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]-diphenolato-1$\kappa^4$*O*,*N*,*N*′,*O*′}-$\mu$-nitrido-1:2$\kappa^2$*N*:*N*-chromium(V)rhodium(I), $[CrRh(C_{16}H_{14}N_2O_2)ClN(C_8H_{12})]$. The Cr—N bond of 1.5936 (14) Å is elongated by only 0.035 Å compared to the terminal Cr—N bond in the precursor. The nitride bridge is close to being linear [173.03 (9)°] and the Rh—N bond of 1.9594 (14) Å is very short for a monodentate nitrogen-donor ligand, indicating significant $\pi$-acceptor character of the Cr≡N group.

## Comment

Heterobimetallic nitride complexes are of interest as precursors for interstitial heterobimetallic nitride phases which have interesting catalytic properties. One such example is $Co_3Mo_3N$, which is a very efficient catalyst in the Haber–Bosch process (Jacobsen, 2000). The number of structurally characterized heterobimetallic nitride-bridged complexes is low, with only 64 reported examples [Cambridge Structural Database (CSD) (Allen, 2002), Version 5.31 of November 2009] despite the fact that this class of compounds dates back to 1968 when $(PEt_2Ph)_3Cl_2Re(\mu\text{-}N)PtCl_2(PEt_3)$ was described by Chatt & Heaton (1968).

As is the case for the mononuclear nitride complexes, the chemistry of heterobimetallic nitride-bridged complexes is strongly dominated by the second- and third-row transition metals. More than 90% of the known systems are, thus, derived from the very stable nitride complexes of rhenium and osmium. Much of this chemistry has been developed by Strähle and Abram who have demonstrated that terminal nitride complexes, not unexpectedly, form bridged systems with typical Lewis acids, such as $ZnX_2$ ($X$ = Cl, Br, I), $GaCl_3$, $SnCl_4$ and $VOCl_2$ (Hagenbach & Strähle, 1999; Abram *et al.*, 1999; Gauch & Strähle, 2000; Haug & Strähle, 1998). Less intuitively, it has been found that the coordination of a low-valent platinum group metal centre to a terminal nitride complex is quite general, and a large fraction of the reported heterobimetallic nitride-bridged complexes contain Co, Pd, Rh, Ru, Pt or Ir (Crevier *et al.*, 1998; Schwarz & Strähle, 2002, 2003; Zheng *et al.*, 2000; Leung *et al.*, 1996; Schwarz *et al.*, 2003). For the first-row transition metals only, titanium and vanadium are known to make heterobimetallic nitride-bridged complexes, exemplified by $(PMe_2Ph)_3(CH_3CN)ClRe(\mu\text{-}N)TiCl_5$ (Gauch *et al.*, 2000) and $(Me_3SiO)_3V(\mu\text{-}N)PtMe(PEt_3)_2$ (Doherty & Critchlow, 1987), respectively. While terminal nitride complexes of chromium and manganese have been known for almost 30 years, no examples have been isolated where these function as a ligand towards another metal, although one example of a linear chromium nitride chain



(I)

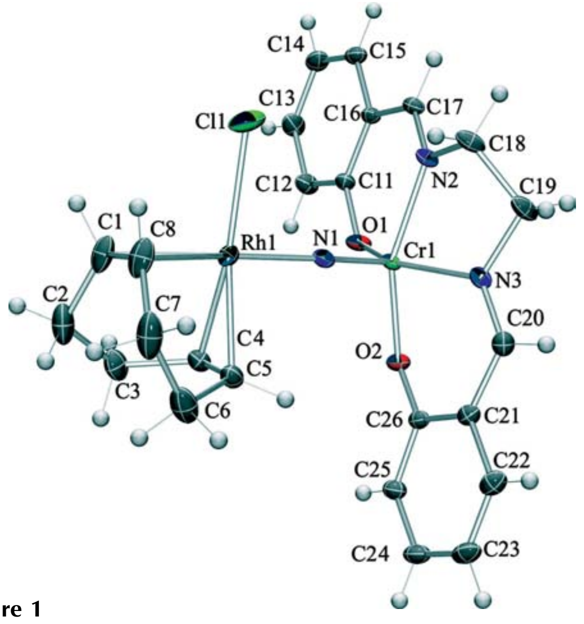


**Figure 1**
A view of the molecular structure of Cr(salen)($\mu$-N)RhCl(COD), (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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compound has been reported by Tsuchimoto *et al.* (2001). We have recently devised a general route to chromium(V) nitride complexes based on nitrogen transfer from the easily accessible Mn(N)(salen) {salen is 2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolate} to labile chromium acceptors (Birk & Bendix, 2003; Bendix, 2003; Bendix *et al.*, 2005). Among the chromium(V) nitride complexes which can be prepared by this route is Cr(N)(salen), which previously was only accessible in modest quantities through a cumbersome photolysis of the chromium(III) precursor $Cr(N_3)$(salen) (Arshankow & Poznjak, 1981; Bendix *et al.*, 1998). We have found that Cr(N)(salen) reacts directly with $[RhCl(COD)]_2$ (COD is 1,5-cyclooctadiene) to yield the title complex, (I), which is the first example of the Cr≡N moiety functioning as a ligand towards another metal.

The molecular structure of (I) is depicted in Fig. 1. Bond lengths are summarized in Table 1. The two metals are connected by a nearly linear [173.03 (9)°] nitride bridge. The Cr≡N is elongated from 1.559 (2) Å in Cr(N)(salen) (Bendix *et al.*, 1998; Table 2) to 1.5936 (14) Å in (I). Despite this modest change in bond length, the N—Rh bond of 1.9594 (14) Å is very short for a monodentate nitrogen-donor ligand bonded to $Rh^{I}$. In $\eta^1$-($^{i}Pr_2$tacn)RhCl(COD) (tacn is 1,4,7-triazacyclononane), where the fourth donor is a secondary amine, the Rh—N bond length is 2.156 (4)/2.145 (6) Å (Gott *et al.*, 2004) and in *cis*-$Rh(CO)_2Cl$(py) (py is pyridine) the Rh—N bond length is 2.122 (7) Å (Heaton *et al.*, 1998). The short Rh—N bond in (I) is in line with the findings of Mayer and co-workers, who noted that the similarity between the frontier orbitals on Os≡N [the LUMO (lowest unoccupied molecular orbital) being a *d*–*p* $\pi^*$ MO] and on carbon monoxide (*p*–*p* $\pi^*$ MO) could explain, through $\pi$-backbonding, the anomalously short bond lengths when $Os(N)Cl_2$(Tp) [Tp = hydrotris(1-pyrazolyl)borate] interacted with low-valent cobalt or platinum centres (Crevier *et al.*, 1998). Only two other examples of nitride bridges to RhCl(COD) have been reported. In $[(Me_2PhP)_3Cl_2Re(\mu$-N)RhCl(COD)], the Rh—N bond length is comparable [1.956 (6) Å] to that of (I) (Schwarz & Strähle, 2003), while it is shorter still [1.846 (6) Å] in $[(Ph_3Sb)_2Cl_3Os(\mu$-N)RhCl(COD)] (Schwarz *et al.*, 2004). It thus appears that the $\pi$-acceptor strength of the *M*≡N fragments depends significantly on the oxidation state of the metal. On the other hand, the $[Re(N)Cl_2(Me_2PhP)_3]$ complex coordinates to the rhodium and iridium fragments (Rh/Ir)Cl(COD) with bond lengths the same within experimental error, demonstrating the nature of the electron-rich metal centre to be of minor significance for the $\pi$-backbonding to the nitride complex. For comparison, bond lengths and angles in nitride-bridged complexes of (Rh/Ir)Cl(COD) are summarized in Table 3.

## Experimental

Cr(N)(salen) (Birk & Bendix, 2003) and $[RhCl(COD)]_2$ (Giordano & Crabtree, 1979) were prepared as described in the literature. $CH_2Cl_2$ and tetrahydrofuran (THF) were purchased from Aldrich and used without any further purification. Compound (I) was prepared by dissolving $[Rh(COD)Cl]_2$ (16.9 mg) in $CH_2Cl_2$ (12.5 ml), which was added to a solution of Cr(N)(salen) (50 mg) in $CH_2Cl_2$ (12.5 ml) under stirring. This solution was heated to near boiling and then filtered. The filtrate was allowed to precipitate over a period of 3 d. Crystals suitable for X-ray diffraction studies were collected on a glass filter and washed with cold THF. The yield was 27.6 mg (69%).

*Crystal data*

$[CrRh(C_{16}H_{14}N_2O_2)ClN(C_8H_{12})]$
$M_r = 578.84$
Monoclinic, $P2_1/c$
$a = 12.6140$ (13) Å
$b = 15.1085$ (14) Å
$c = 12.6704$ (17) Å
$\beta = 107.259$ (10)°
$V = 2306.0$ (4) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.33$ mm$^{-1}$
$T = 122$ K
0.32 × 0.09 × 0.09 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: integration (Gaussian; Coppens, 1970)
$T_{\min} = 0.718$, $T_{\max} = 0.929$
77914 measured reflections
9382 independent reflections
7611 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.067$
$S = 1.06$
9382 reflections
289 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.92$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.98$ e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Rh1—N1 | 1.9594 (14) | Cr1—N1 | 1.5936 (14) |
| Rh1—Cl1 | 2.3644 (6) | Cr1—O1 | 1.8870 (11) |
| Rh1—C1 | 2.1921 (18) | Cr1—O2 | 1.9063 (11) |
| Rh1—C8 | 2.1744 (18) | Cr1—N2 | 2.0017 (13) |
| Rh1—C4 | 2.1065 (16) | Cr1—N3 | 2.0091 (14) |
| Rh1—C5 | 2.1126 (17) | | |

**Table 2**
Comparative geometric parameters (Å) for a nitride-bridged *versus* terminal nitride–chromium–salen complex.

| | (salen)Cr($\mu$-N)RhCl(COD), (I)$^a$ | Cr(N)(salen)$^b$ |
|---|---|---|
| Cr≡N | 1.5936 (14) | 1.559 (2) |
| Cr—O | 1.8870 (11)–1.9063 (11) | 1.910 (2)–1.913 (2) |
| Cr—N | 2.0017 (13)–2.0091 (14) | 2.017 (2)–2.019 (2) |
| Cr-oop$^c$ | 0.4827 (7) | 0.501 (1) |

Notes: (*a*) present work; (*b*) Bendix *et al.* (1998); (*c*) oop = out-of-plane.

All H atoms were found in a difference Fourier map, then included in the refinement in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (aromatic), 0.99 (methylene) or 1.00 Å (methine), and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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**Table 3**
Comparative geometric parameters (Å, °) for nitride-bridged complexes of (Rh/Ir)Cl(COD).

| | Rh/Ir—N | Rh/Ir—Cl | Rh/Ir—C | $M$≡N—Rh/Ir |
|---|---|---|---|---|
| (salen)Cr($\mu$-N)-RhCl(COD)[a] | 1.9594 (14) | 2.3644 (6) | 2.1065 (16)–2.1921 (18) | 173.03 (9) |
| $(Me_2PhP)_3Cl_2Re$-($\mu$-N)RhCl(COD)[b] | 1.956 (6) | 2.373 (3) | 2.10 (1)–2.17 (1) | 174.8 (4) |
| $(Ph_3Sb)_2Cl_3Os$($\mu$-N)-RhCl(COD)[c] | 1.846 (6) | 2.337 (3) | 2.138 (10)–2.274 (11) | 175.3 (5) |
| $(Me_2PhP)_3Cl_2Re$-($\mu$-N)IrCl(COD)[d] | 1.962 (8) | 2.342 (3) | 2.10 (1)–2.18 (1) | 173.8 (4) |
| $[O_3Os(\mu\text{-N})IrCl\text{-}(COD)]^-$[d] | 1.978 (7) | 2.353 (3) | 2.09 (1)–2.142 (9) | 161.8 (4) |
| $[Rh(COD)Cl]_2$[e] | | 2.402 (1)–2.421 (1) | 2.097 (6)–2.126 (6) | |

Notes: (*a*) present work; (*b*) Schwarz & Strähle (2003); (*c*) Schwarz *et al.* (2004); (*d*) Schwarz *et al.* (2003); (*e*) De Ridder & Imhoff (1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3042). Services for accessing these data are described at the back of the journal.

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