metal-organic compounds

The *trans* influence in *mer*-trichloronitridobis(triphenylarsine)-ruthenium(VI)

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The title compound, *mer*-[RuCl$_3$N(C$_{18}$H$_{15}$As)$_2$], is the first structurally characterized example of a nitride complex in which ruthenium is six-coordinated to monodentate ligands only. The Ru≡N bond length [1.6161 (15) Å] is relatively long, and the *trans* influence of the nitride ligand is reflected by the difference between the Ru—Cl$_{trans}$ and Ru—Cl$_{cis}$ bond lengths [0.1234 (4) Å]. The N—Ru—Cl$_{trans}$ axis is sited on a twofold axis.

Comment

Ruthenium–nitride complexes have been well known since 1972 (Griffith & Pawson, 1972). However, all of the structurally characterized Ru≡N complexes with monodentate auxiliary ligands are square pyramidal and five-coordinate (Phillips & Skapski, 1975; Collison *et al.*, 1981; Sharpley *et al.*, 1988; Liang & Sharpley, 1996), which provides a qualitative indication of the strong *trans* influence of the nitride ligand. In order to obtain a good quantitative measure of the *trans* influence unperturbed by the steric requirements of polydentate ligands, we have undertaken a study of *mer*-[RuNCl$_3$(AsPh$_3$)$_2$], (I).
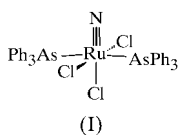
The structure of (I) consists of discrete monomers and the coordination geometry (Fig. 1 and Table 1) is distorted octahedral. The three chloride ligands are arranged in a meridional configuration in which one chloride ligand is *trans* to the nitride, as proposed by Pawson & Griffith (1975).

The Ru≡N bond length of 1.6161 (15) Å is relatively long compared with that in other ruthenium–nitride compounds and is only exceeded by the distance in bis(1,2-benzenedithiolato)nitridoruthenate(VI) [1.613 (5) and 1.621 (5) Å in

two independent molecules; Sellmann *et al.*, 1997] and in *μ*-oxo-tetrakis(2,5-dimethyl-2,5-hexanediamine-*N,N'*)nitridodiruthenium(VI) [1.66 (1) Å; Chiu *et al.*, 1996].

The Ru—As bond length of 2.5533 (3) Å is the longest reported Ru—As bond length in ruthenium compounds with AsPh$_3$ and related ligands. Note that arsine ligands support ruthenium in oxidation states ranging from Ru^0 in [Ru(AsPh$_3$)(CO)$_4$] (Martin *et al.*, 1983) to Ru^{VI} in ruthenium–nitride complexes such as (I).

In five- and six-coordinate complexes with strong π-donor ligands, such as oxide and nitride, the central metal is invariably displaced out of the plane of the equatorial ligands towards the multiply bonded ligand. This phenomenon is much less pronounced in six-coordinate compounds, probably as a result of steric interactions. The N—Ru—Cl1 and N—Ru—As angles of 93.325 (7) and 93.59 (1)° in (I) indicate that the Ru atom lies 0.1483 (2) Å above the equatorial plane defined by the two Cl and two As atoms. This deviation is less than half the value of the out-of-plane distances seen in five-coordinate nitride compounds, where the deviations range from 0.34 Å in [MoN(N$_3$)$_4$]$^-$ (Dehnicke *et al.*, 1980) to 0.768 Å in [TcN(Se$_2$C=C(CN)$_2$)]$^{2-}$ (Abram *et al.*, 1991). In (I), the Ru—Cl$_{trans}$ bond length [2.5020 (4) Å] is longer than the Ru—Cl$_{cis}$ bond length [2.3786 (3) Å], but this *trans* influence is relatively small compared with that observed for other six-coordinate nitride complexes (Table 2). This smaller influence may be a result of the small out-of-plane displacement of the Ru atom in (I), which reflects the steric bulk of the AsPh$_3$ ligands and the concomitant strain involved in closing all angles involving the arsine ligands.

The closely related compound *mer*-[Ru(NO)Cl$_3$(AsPh$_3$)$_2$] (Souza *et al.*, 1995) is isostructural with (I). The geometric parameters of these two complexes are almost identical (Table 3), but the nitrosyl ligand does not exert any *trans* influence. This result is paralleled for first-row transition
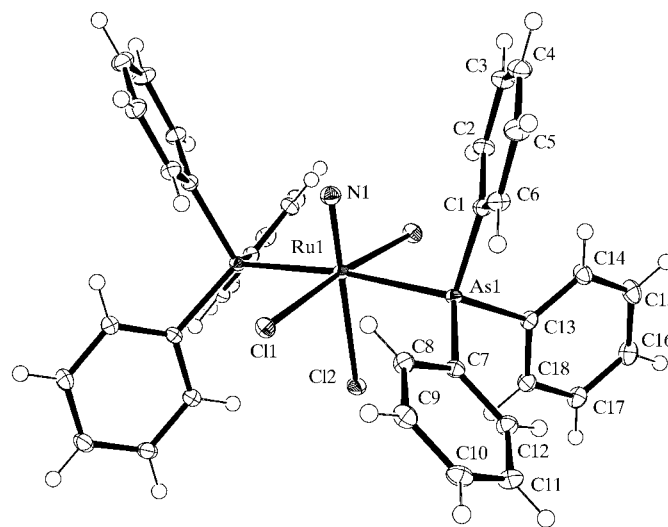

Figure 1
A view of the molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

metals by the strong *trans* influence found in $[Mn(N)(CN)_5]^{3-}$ [0.253 (7) Å; Bendix *et al.*, 2000] and the absence of any *trans* influence in $[Mn(NO)(CN)_5]^{3-}$ [0.03 (1) Å; Tullberg & Vannerberg, 1967]. These findings reflect the general rule that, while strong π-donor ligands exert a *trans* influence, π-acceptors do not (Lyne & Mingos, 1995).

Importantly, the steric demands of the AsPh$_3$ ligand shield the nitride ligand in (I) from intermolecular interactions.
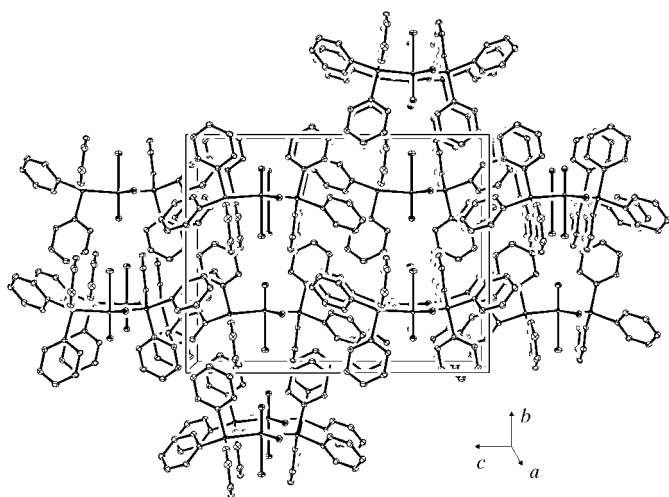

Figure 2
The crystal packing, showing the parallel and antiparallel Ru≡N directions parallel to the *b* axis. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Accordingly, the packing (Fig. 2) is governed by the arrangement of the phenyl groups of the AsPh$_3$ ligands, resulting in several relatively short intermolecular C···C distances [3.6220 (1)–3.9130 (1) Å]. The rhombicity of the molecules is mirrored in the packing; all Ru≡N vectors are parallel (or antiparallel) and all As—As vectors are parallel. The packing thus explains the strong dichroism of the solid compound and makes it a good candidate for polarized single-crystal absorption and luminescence spectroscopy (Cowman *et al.*, 1976; Lam *et al.*, 1993) on an unperturbed Ru≡N moiety.

Experimental

Compound (I) was prepared according to the method described by Pawson & Griffith (1975). Crystals were grown by adding a solution of (Bu$_4$N)[RuNCl$_4$] in methanol to a solution of excess AsPh$_3$ in acetone at room temperature and allowing slow evaporation of the solvents. The crystals are markedly dichroic (red and yellow).

Crystal data

[RuCl$_3$N(C$_{18}$H$_{15}$As)$_2$]
$M_r = 833.87$
Monoclinic, $C2/c$
$a = 12.0020$ (4) Å
$b = 14.5630$ (9) Å
$c = 18.526$ (2) Å
$\beta = 92.882$ (5)°
$V = 3234.0$ (4) Å^3
$Z = 4$

$D_x = 1.713$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 589 reflections
$\theta = 2.2–35.0°$
$\mu = 2.79$ mm^{-1}
$T = 122$ (1) K
Prism, red and yellow
$0.27 \times 0.18 \times 0.14$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: Gaussian integration (Coppens, 1970)
  $T_{min} = 0.462$, $T_{max} = 0.877$
55 021 measured reflections

7120 independent reflections
6361 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 35.0°$
$h = -19 \rightarrow 19$
$k = -23 \rightarrow 23$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.052$
$S = 1.09$
7120 reflections
196 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 4.8314P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	1.6161 (15)	Ru1—Cl1	2.3786 (3)
Ru1—As1	2.5533 (3)	Ru1—Cl2	2.5020 (4)
N1—Ru1—Cl1	93.325 (7)	N1—Ru1—As1	93.59 (1)
Cl1—Ru1—Cl1^i	173.350 (15)	Cl1—Ru1—As1	94.047 (8)
N1—Ru1—Cl2	180.0	Cl2—Ru1—As1	86.41 (1)
Cl1—Ru1—Cl2	86.675 (7)	As1—Ru1—As1^i	172.812 (7)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2
Comparative geometric parameters (Å, °) for selected six-coordinate nitride complexes.

Complex	Average			
	$M\equiv N$	$M-X_{trans}$	$M-X_{cis}$	$N\equiv M-L_{eq}$
mer-[RuNCl$_3$(AsPh$_3$)$_2$][a]	1.6161 (15)	2.5020 (4)	2.3786 (3)	93.325 (7)
				−93.59 (1)
fac-[OsNCl$_3$(dpae)][b]	1.68 (2)	2.507 (5)	2.377 (5)	86.5 (5)
				−102.6 (5)
[OsNCl$_5$]$^{2-}$ [c]	1.614 (13)	2.605 (4)	2.363 (4)	95.44 (6)
				−97.5 (5)
[OsN(CN)$_5$]$^{2-}$ [d]	1.647 (7)	2.353 (8)	2.080 (8)	93.3 (3)
				−99.4 (3)
[ReN(NCS)$_5$]$^{2-}$ [e]	1.657 (12)	2.307 (12)	2.023 (8)	95.5 (4)
				−96.8 (5)
mer-[ReNBr$_2$(PMe$_2$Ph)$_3$][f]	1.667 (6)	2.795 (1)	2.587 (1)	91.0 (2)
				−103.6 (2)

Notes: (*a*) present work; (*b*) Lam *et al.* (1993) [dpae is bis(diphenylarsino)ethane]; (*c*) Bright & Ibers (1969); (*d*) Che *et al.* (1989); (*e*) Carrondo *et al.* (1978); (*f*) Schmidt-Brücken & Abram (2001).

Table 3
Comparative geometric parameters (Å, °) for *mer*-[RuNCl$_3$(AsPh$_3$)$_2$] and *mer*-[Ru(NO)Cl$_3$(AsPh$_3$)$_2$].

	mer-[RuNCl$_3$(AsPh$_3$)$_2$]	*mer*-[Ru(NO)Cl$_3$(AsPh$_3$)$_2$]
Ru—N	1.6161 (15)	1.729 (7)
Ru—Cl	2.3786 (3)	2.384 (1)
Ru—Cl	2.5020 (4)	2.346 (2)
N—Ru—Cl	93.325 (7)	90.0 (1)
N—Ru—As	93.59 (1)	91.5 (1)

H atoms were found in a difference Fourier map and were included in the refinement at idealized positions, riding on their parent atoms (C—H = 0.93 Å).

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Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EvalCCD* (Duisenberg, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997) and *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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