Rhodium(III)-Assisted Nucleophilic Addition of Ammonia to Metal-Bound Benzyl Cyanide: Crystal Structures of *mer*-$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5CH_3$ and *mer*-$[RhCl_3\{PhCH_2C(NH_2)=NH\}_3]$

Vadim Yu. Kukushkin,*[a] Igor V. Ilichev,[a] Gabriele Wagner,[b] Mikhail D. Revenco,[c] Viktor H. Kravtsov,[d] and Kinga Suwinska[e]

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Heating of $[RhCl_3(MeCN)_3]$ in benzyl cyanide at 100 °C gives the substitution product *mer*-$[RhCl_3(PhCH_2CN)_3]$ (90% yield), whose recrystallization from an acetone/toluene mixture leads to formation of the toluene solvate *mer*-$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5Me$. The crystal structure of the latter, determined by X-ray single-crystal diffractometry, shows an unusual self-assembly due to intermolecular CH···Cl hydrogen bonding with concomitant clathration of toluene. Diffusion of ammonia into a solution of *mer*-$[RhCl_3(PhCH_2CN)_3]$ in neat benzyl cyanide brings about a facile rhodium(III)-assisted addition of NH_3 to the coordinated nitrile species to produce the amidine complex *mer*-$[RhCl_3\{PhCH_2C(NH_2)=NH\}_3]$ (83% yield). Both starting material and the product were characterized by elemental analyses, FAB-MS, IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The crystal structure of *mer*-$[RhCl_3\{PhCH_2C(NH_2)=NH\}_3]$ provides the first example of a rhodium(III) complex with a monodentate amidine ligand.

Introduction

The application of organonitrile transition metal complexes as synthons for preparation of a great variety of new compounds by the addition of nucleophiles − such as water/hydroxide, amines with sp^3 or sp^2 nitrogen atoms or mercaptans − to the carbon atom of the nitrile group has recently been reviewed comprehensively by Michelin and colleagues.[1] Our own research in this field has so far been focused on the hydrolysis of nitriles coordinated to a Rh−Rh unit to give a novel type of metallacycle,[2] addition of ethylenediamine to $[PtCl_2(PhCN)_2]$ to afford $[Pt(NH{=}C(Ph)NHCH_2CH_2NH_2)_2]^{2+}$, a complex that contains two unusual seven-membered organic metallacycles bound to the same platinum(II) center,[3] and the addition of nucleophiles with concerted cyclization of cyanoguanidine that yielded a novel type of azametallacycle, *cis*-$[(PPh_3)_2Pt\{NHC(Nuc){=}NC(NH_2){=}NH\}][BPh_4]$[4] and facile hydrolysis of organonitriles in platinum(IV) complexes to yield $[Pt^{IV}]{-}NH_3$ species.[5] Furthermore, we have recently observed a reaction between platinum(IV),[6−9] rhenium(IV)[10] and rhodium(III)[11] nitrile complexes and ketoximes, aldoximes, *vic*-dioximes, or dialkylhydroxylamines which led to isolation of iminoacylated compounds containing $[M]{-}\{NH{=}C(R)ON{=}CR'R''\}$,[6,9−11] $[M]{-}\{NH{=}C(R)ON{=}C(R'){-}C(R'){=}NOH\}$[7] or $[M]{-}\{NH{=}C(R)ONR'_2\}_2]$[8] moieties.

As part of our continuing interest in ligand reactivity in general,[12−15] and in reactions of coordinated nitriles[2−11] in particular we have now studied the ammination of the rhodium(III) complex *mer*-$[RhCl_3(PhCH_2CN)_3]$ by NH_3 giving the amidine complex *mer*-$[RhCl_3\{PhCH_2C(NH_2){=}NH\}_3]$; these results, along with crystal structures of both starting material and the addition product, are reported herein.

Results and Discussion

There is much current interest in the chemistry of amidine/amidato transition metal complexes as evidenced, in particular, by the large number of papers published and also by detailed reviews written on the subject.[16,17] In the vast majority of cases complexes containing $RC(NH_2){=}NH$ species are prepared by direct addition of the *amidine* to a complex. Metal-assisted reactions of *coordinated organonitriles* and ammonia lead to a very attractive route for preparation of complexes containing $RC(NH_2){=}NH$ ligands. Despite the isolation of the first amidine metal compound formulated as $[Pt\cdot 2MeCN\cdot 4NH_3]Cl_2$,[18] the proposal of its amidine structure[19] and the first crystallographic determination of the amidine complex, $[Pt(NH_3)_2$-

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[a] Department of Chemistry, St. Petersburg State University,
Universitetsky Pr. 2, 198904 Stary Petergof, Russian Federation
Fax: (internat.) + 7-812/428-6939,
E-mail: kukushkin@VK2100.spb.edu
[b] Complexo I, Instituto Superior Técnico, Av. Rovisco Pais,
1049−001 Lisbon, Portugal
[c] Department of Chemistry, State University of Moldova,
MD 2009, Chisinau, Republic of Moldova
[d] Institute of Applied Physics, Academy of Sciences,
MD 2028, Chisinau, Republic of Moldova
[e] Institute of Physical Chemistry of the Polish Academy of Sciences, Department of Physico-Chemistry of Supramolecular Complexes
ul. Kasprzaca 44/52, 01-224, Warzawa, Poland

$(MeC(NH_2)=NH)_2]^{2+}$,[20] this exciting chemistry was not developed much further, although additions of *substituted* amines to RCN ligands are fairly well-documented.[1] Besides the above-mentioned work[18] on the addition of NH_3 to the acetonitrile complex $[PtCl_2(MeCN)_2]$, attention should be drawn to ammination by liquid ammonia of $[Co(NH_3)_5(NCR)]^{3+}$ complexes[21] and addition of NH_3 to acetonitrile in a cationic tungsten compound.[22]

Although the kinetics and mechanisms of the reaction of metal-bound organonitriles and *primary* amines have been investigated in a limited number of cases,[1] it is generally believed[23–26] that the reaction takes place by nucleophilic attack of the amine N atom to the nitrile carbon, which is electrophilically activated by its ligation to a metal center; metal ions in high oxidation states should provide a stronger electrophilic activation towards nucleophiles thus facilitating the addition. For this study we chose a benzyl cyanide complex of rhodium(III) for the following reasons: first, it has been proved that the rhodium(III) ion provides a high degree of activation of an organonitrile. Indeed, a ca. 10^6-fold increase in the rate of base-catalyzed hydration of RCN has been reported when these species are coordinated to a Rh^{III} center.[27] Second, the electron-acceptor benzyl group of the nitrile, in contrast to the electron-donor methyl in $[RhCl_3(MeCN)_3]$, should provide an additional activation of the C atom.

The starting material for this work, *mer*-$[RhCl_3(PhCH_2CN)_3]$, was prepared in high (90%) yield by a route described earlier for phenyl- and benzyl cyanide complexes of platinum(II),[28] i.e. by heating of the easily obtained acetonitrile complex $[RhCl_3(MeCN)_3]$[29] in neat benzyl cyanide at 100 °C in an open beaker. It has been suggested that both the large excess of $PhCH_2CN$ and removal of MeCN from the reaction mixture at high temperature drive the reaction. Recrystallization of *mer*-$[RhCl_3(PhCH_2CN)_3]$ from an acetone/toluene mixture gave a toluene solvate *mer*-$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5CH_3$ that was characterized by X-ray single-crystal diffractometry.

The coordination polyhedron of the complex is a slightly distorted octahedron (Figure 1) with both the $PhCH_2CN$ and chloride ligands in *mer* positions. The *mer*-configuration of the rhodium(III) compound persists also in $CDCl_3$ solution as evidenced by observation of the two non-equivalent $PhCH_2CN$ species in a 1:2 ratio in ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental Section).

The two mutually *trans* Rh−Cl bonds [Rh−Cl(1) and Rh−Cl(3)] are equal and slightly longer than the third one [Rh−Cl(2)] (Table 1) thus reflecting a higher ground-state *trans*-influence of the Cl^- ligand than the benzyl cyanide one. A higher *trans*-influence of the other nitrile, i.e. acetonitrile, was also detected in *mer*-$[RhCl_3(MeCN)_3]\cdot MeCN$,[29] while the *trans*-influence of RCN and Cl^- ligands are almost the same for (organonitrile)Pt^{II} complexes.[30–33] The geometry and bond lengths in $PhCH_2CN$ ligands (Table 1) are normal and agree well with the previously reported data on organonitrile Rh^{III} complexes.[33–41]

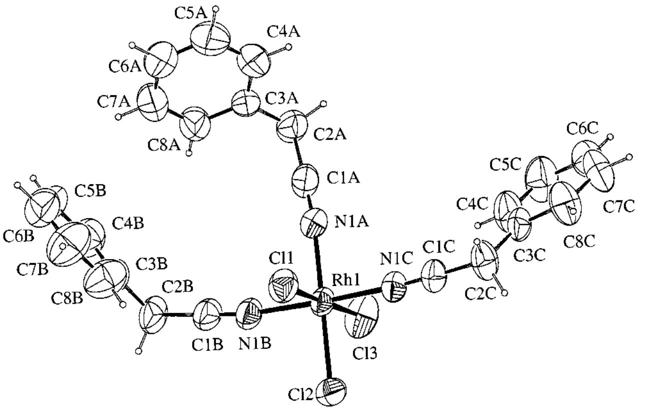

Figure 1. ORTEP drawing of *mer*-$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5CH_3$ with atomic numbering scheme

Table 1. Bond lengths (Å) and angles (°) in *mer*-$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5Me$

Rh(1)−N(1A)	2.021(4)	C(1B)−C(2B)	1.468(7)
Rh(1)−N(1B)	1.993(4)	C(2B)−C(3B)	1.520(7)
Rh(1)−N(1C)	1.982(4)	C(3B)−C(4B)	1.372(7)
Rh(1)−Cl(1)	2.326(1)	C(3B)−C(8B)	1.352(9)
Rh(1)−Cl(2)	2.302(1)	C(4B)−C(5B)	1.382(9)
Rh(1)−Cl(3)	2.326(1)	C(5B)−C(6B)	1.33(1)
N(1A)−C(1A)	1.132(6)	C(6B)−C(7B)	1.36(1)
C(1A)−C(2A)	1.456(7)	C(7B)−C(8B)	1.380(9)
C(2A)−C(3A)	1.515(7)	N(1C)−C(1C)	1.130(5)
C(3A)−C(4A)	1.373(7)	C(1C)−C(2C)	1.463(6)
C(3A)−C(8A)	1.368(7)	C(2C)−C(3C)	1.516(7)
C(4A)−C(5A)	1.390(9)	C(3C)−C(4C)	1.365(7)
C(5A)−C(6A)	1.347(9)	C(3C)−C(8C)	1.378(7)
C(6A)−C(7A)	1.353(9)	C(4C)−C(5C)	1.368(8)
C(7A)−C(8A)	1.373(8)	C(5C)−C(6C)	1.383(9)
N(1B)−C(1B)	1.125(6)	C(6C)−C(7C)	1.358(9)
		C(7C)−C(8C)	1.369(8)
Cl(1)−Rh(1)−Cl(2)	90.40(5)	C(2B)−C(3B)−C(8B)	121.8(6)
Cl(1)−Rh(1)−Cl(3)	179.03(6)	C(4B)−C(3B)−C(8B)	118.5(6)
Cl(1)−Rh(1)−N(1A)	90.62(13)	C(2C)−C(3C)−C(4C)	124.2(4)
Cl(1)−Rh(1)−N(1B)	89.89(13)	C(2C)−C(3C)−C(8C)	117.6(5)
Cl(1)−Rh(1)−N(1C)	89.20(13)	C(4C)−C(3C)−C(8C)	118.2(5)
Cl(2)−Rh(1)−Cl(3)	90.48(6)	C(3A)−C(4A)−C(5A)	120.1(6)
Cl(2)−Rh(1)−N(1A)	178.54(12)	C(3B)−C(4B)−C(5B)	120.6(6)
Cl(2)−Rh(1)−N(1B)	91.57(13)	C(3C)−C(4C)−C(5C)	121.4(5)
Cl(2)−Rh(1)−N(1C)	90.40(13)	C(4A)−C(5A)−C(6A)	120.1(7)
Cl(3)−Rh(1)−N(1A)	88.51(13)	C(4B)−C(5B)−C(6B)	119.5(7)
Cl(3)−Rh(1)−N(1B)	90.49(13)	C(4C)−C(5C)−C(6C)	119.6(6)
Cl(3)−Rh(1)−N(1C)	90.38(13)	C(5A)−C(6A)−C(7A)	120.3(7)
N(1A)−Rh(1)−N(1B)	87.39(16)	C(5B)−C(6B)−C(7B)	121.3(8)
N(1A)−Rh(1)−N(1C)	90.66(16)	C(5C)−C(6C)−C(7C)	119.6(6)
N(1B)−Rh(1)−N(1C)	177.84(18)	C(6A)−C(7A)−C(8A)	120.0(7)
Rh(1)−N(1A)−C(1A)	173.2(4)	C(6B)−C(7B)−C(8B)	118.8(8)
Rh(1)−N(1B)−C(1B)	172.2(5)	C(6C)−C(7C)−C(8C)	120.2(7)
Rh(1)−N(1C)−C(1C)	176.1(4)	C(3A)−C(8A)−C(7A)	121.2(6)
N(1A)−C(1A)−C(2A)	177.9(6)	C(3B)−C(8B)−C(7B)	121.2(7)
N(1B)−C(1B)−C(2B)	179.6(7)	C(3C)−C(8C)−C(7C)	121.0(6)
N(1C)−C(1C)−C(2C)	178.7(6)	C(2A)−C(3A)−C(4A)	121.6(5)
C(1A)−C(2A)−C(3A)	111.5(5)	C(2A)−C(3A)−C(8A)	120.2(5)
C(1B)−C(2B)−C(3B)	112.5(5)	C(4A)−C(3A)−C(8A)	118.2(6)
C(1C)−C(2C)−C(3C)	113.7(4)	C(2B)−C(3B)−C(4B)	119.6(5)

The packing diagram (Figure 2) shows that molecules of *mer*-$[RhCl_3(PhCH_2CN)_3]$ are assembled by intermolecular hydrogen bonding C(2)−H···Cl(2) between the methylene group from one molecule and the chloride from the adjacent molecule thus forming polymeric chains. The observed C(2)H···Cl(2) distances are in the range 2.84−2.85 Å indicating rather weak interactions [the combined contact radius

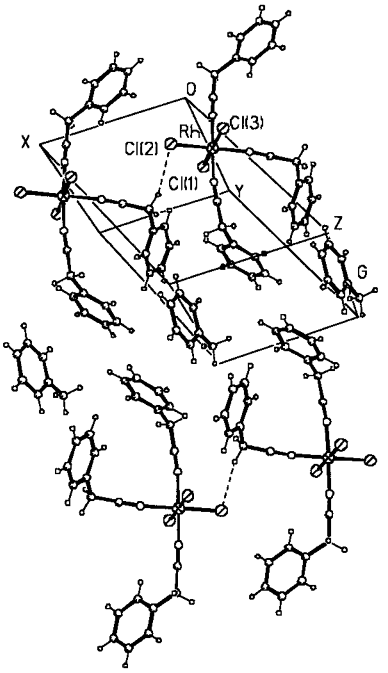

Figure 2. Packing diagram for *mer*-[$RhCl_3(PhCH_2CN)_3$]·1/2 $C_6H_5CH_3$ indicating hydrogen bonding pattern

is H(1.20) + Cl(1.75) = 2.95 Å[42]].[29] Furthermore, the unit cell of *mer*-[$RhCl_3(PhCH_2CN)_3$]·1/2 C_6H_5Me contains half a molecule of clathrated and disordered toluene. The latter has no contacts less than the sum of the van der Waals radii with the *mer*-[$RhCl_3(PhCH_2CN)_3$] molecule. It is worthwhile to mention that clathration of the solvent was observed in the case of the analogous complex *mer*-[$RhCl_3(MeCN)_3$]·MeCN[29] that is also assembled into infinite chains by CH···Cl hydrogen bonding. These two observations together point to the need for a study on the self-assembly/clathration in similar systems. In fact, self-assembly of metal complexes by hydrogen bonding is the rapidly developing area of paramount importance for crystal engineering and material science[43−45] and it is likely − from that viewpoint − that the observation of H-bonding in the (organonitrile)Rh^{III} compounds with concomitant clathration of solvents deserves further investigations.

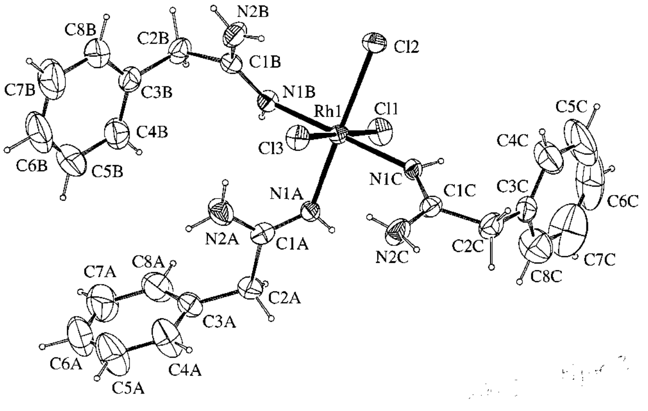

Figure 3. ORTEP drawing of *mer*-[$RhCl_3\{PhCH_2C(NH_2)=NH\}_3$] with atomic numbering scheme

Diffusion of ammonia into a solution of *mer*-[$RhCl_3(PhCH_2CN)_3$] in neat benzyl cyanide at 20−25 °C for one day led to the addition of NH_3 across the C≡N bond giving the rhodium(III) complex containing neutral amidine ligands *mer*-[$RhCl_3\{PhCH_2C(=NH)(NH_2)\}_3$] which was isolated in good yield. The structure of the product of ammination has been determined by X-ray crystallography (Figure 3).

The coordination at rhodium is octahedral with small deviations from ideal geometry. The amidine species are coordinated through their imino nitrogens, adopting the *mer*-configuration which remains in $CDCl_3$ solution (see Experimental Section). The $PhCH_2C(NH_2)=NH$ ligands are in a *Z*-configuration in the solid state. Moreover, no evidence for existence of an *E*-conformation in solution can be derived from the NMR spectroscopic data. The HN=C [1.239(5)−1.285(5) Å] and H_2N-C [1.305(5)−1.330(5) Å] bonds (Table 2) lie in the normal range.[46] Hydrogen atoms from all three amidine species are involved in both *intra*-)

Table 2. Bond lengths (Å) and angles (°) in *mer*-[$RhCl_3\{PhCH_2C(NH_2)=NH\}_3$]

Rh(1)−N(1A)	1.996(3)	C(1B)−C(2B)	1.502(5)
Rh(1)−N(1B)	2.023(3)	C(2B)−C(3B)	1.467(6)
Rh(1)−N(1C)	2.018(3)	C(3B)−C(4B)	1.364(6)
Rh(1)−Cl(1)	2.313(1)	C(3B)−C(8B)	1.370(6)
Rh(1)−Cl(2)	2.367(1)	C(4B)−C(5B)	1.354(7)
Rh(1)−Cl(3)	2.355(1)	C(5B)−C(6B)	1.341(8)
N(1A)−C(1A)	1.239(5)	C(6B)−C(7B)	1.351(8)
N(2A)−C(1A)	1.323(5)	C(7B)−C(8B)	1.337(7)
C(1A)−C(2A)	1.507(5)	N(1C)−C(1C)	1.285(5)
C(2A)−C(3A)	1.466(6)	N(2C)−C(1C)	1.305(6)
C(3A)−C(4A)	1.334(7)	C(1C)−C(2C)	1.495(5)
C(3A)−C(8A)	1.354(7)	C(2C)−C(3C)	1.469(6)
C(4A)−C(5A)	1.340(8)	C(3C)−C(4C)	1.333(7)
C(5A)−C(6A)	1.332(9)	C(3C)−C(8C)	1.358(6)
C(6A)−C(7A)	1.353(9)	C(4C)−C(5C)	1.351(9)
C(7A)−C(8A)	1.350(8)	C(5C)−C(6C)	1.36(1)
N(1B)−C(1B)	1.285(5)	C(6C)−C(7C)	1.31(1)
N(2B)−C(1B)	1.330(5)	C(7C)−C(8C)	1.340(9)
N(1A)−Rh(1)−N(1C)	89.3(1)	C(7A)−C(8A)−C(3A)	121.8(6)
N(1A)−Rh(1)−N(1B)	88.7(1)	C(1B)−N(1B)−Rh(1)	134.7(3)
N(1C)−Rh(1)−N(1B)	172.1(2)	N(1B)−C(1B)−N(2B)	122.7(4)
N(1A)−Rh(1)−Cl(1)	86.6(1)	N(1B)−C(1B)−C(2B)	121.3(4)
N(1C)−Rh(1)−Cl(1)	85.0(1)	N(2B)−C(1B)−C(2B)	116.0(4)
N(1B)−Rh(1)−Cl(1)	87.3(1)	C(3B)−C(2B)−C(1B)	109.1(4)
N(1A)−Rh(1)−Cl(3)	93.3(1)	C(4B)−C(3B)−C(8B)	118.8(5)
N(1C)−Rh(1)−Cl(3)	94.0(1)	C(4B)−C(3B)−C(2B)	120.2(4)
N(1B)−Rh(1)−Cl(3)	93.7(1)	C(8B)−C(3B)−C(2B)	121.0(4)
Cl(1)−Rh(1)−Cl(3)	179.00(4)	C(5B)−C(4B)−C(3B)	120.4(5)
N(1A)−Rh(1)−Cl(2)	177.1(1)	C(6B)−C(5B)−C(4B)	118.6(6)
N(1C)−Rh(1)−Cl(2)	90.3(1)	C(5B)−C(6B)−C(7B)	122.5(6)
N(1B)−Rh(1)−Cl(2)	91.3(1)	C(8B)−C(7B)−C(6B)	118.4(6)
Cl(1)−Rh(1)−Cl(2)	90.55(4)	C(7B)−C(8B)−C(3B)	121.1(6)
Cl(3)−Rh(1)−Cl(2)	89.56(4)	C(1C)−N(1C)−Rh(1)	138.9(3)
C(1A)−N(1A)−Rh(1)	132.4(3)	N(1C)−C(1C)−N(2C)	123.2(4)
N(1A)−C(1A)−N(2A)	122.2(4)	N(1C)−C(1C)−C(2C)	123.8(4)
N(1A)−C(1A)−C(2A)	120.2(4)	N(2C)−C(1C)−C(2C)	113.0(4)
N(2A)−C(1A)−C(2A)	117.5(4)	C(3C)−C(2C)−C(1C)	114.7(4)
C(3A)−C(2A)−C(1A)	116.5(4)	C(4C)−C(3C)−C(8C)	119.2(5)
C(4A)−C(3A)−C(8A)	119.2(5)	C(4C)−C(3C)−C(2C)	119.9(5)
C(4A)−C(3A)−C(2A)	120.0(5)	C(8C)−C(3C)−C(2C)	120.9(5)
C(8A)−C(3A)−C(2A)	120.8(5)	C(3C)−C(4C)−C(5C)	119.3(7)
C(3A)−C(4A)−C(5A)	119.8(6)	C(4C)−C(5C)−C(6C)	121.0(9)
C(6A)−C(5A)−C(4A)	120.7(7)	C(7C)−C(6C)−C(5C)	118.9(9)
C(5A)−C(6A)−C(7A)	121.1(7)	C(6C)−C(7C)−C(8C)	120.9(9)
C(8A)−C(7A)−C(6A)	117.3(7)	C(7C)−C(8C)−C(3C)	120.7(7)

and *inter*molecular hydrogen bonding with chlorides thus precluding any conclusions about the "pure" ground-state *trans*-influence of $HN{=}C(NH_2)CH_2Ph$ ligands. The crystal structure of *mer*-$[RhCl_3\{PhCH_2C(NH_2){=}NH\}_3]$ is so far the only one for a rhodium(III) complex with monodentate amidines.

In conclusion, it is important to point out that *free* benzyl cyanide does not react with ammonia in $CDCl_3$ at room temperature (proved by ^1H NMR spectroscopy) or on a preparative scale (verified by a synthetic experiment) and these facts imply that the ammonia addition to *mer*-$[RhCl_3(PhCH_2CN)_3]$ is metal-assisted. To the best of our knowledge the ammination of coordinated RCN species in rhodium(III) complexes has not yet been investigated and this is the first example of its kind.

Experimental Section

Materials and Instrumentation: Solvents were obtained from commercial sources and used as received. $[RhCl_3(MeCN)_3]$ was prepared following a published method.[29] C, H and N elemental analyses were carried out by the Microanalytical Service of St. Petersburg State Technological Institute. Melting points were determined on a Kofler table. For TLC, Merck UV 254 SiO_2-plates were used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument as KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

***mer*-$[RhCl_3(PhCH_2CN)_3]$:** $[RhCl_3(MeCN)_3]$ (0.1 g, 0.3 mmol) was dissolved in benzyl cyanide (1.0 mL, 8.7 mmol) and heated at 100 °C for 4 h in an open beaker. After this time the mixture was cooled to 20−25 °C and diethyl ether (20 mL) added dropwise with continuous stirring. The precipitate released was collected on a filter, washed with three portions of Et_2O (each 3 mL)and dried in air at room temperature. Yield: 0.15 g (90%); m.p. 122 °C. − TLC on SiO_2, $R_f = 0.69$ (eluent $CHCl_3/Me_2CO$ = 3:1, v/v). − $C_{24}H_{21}Cl_3N_3Rh$ (560.7): calcd. C 51.4, H 3.7, Cl 19, N 7.5, Rh 18.4; found C 52.3, H 3.7, Cl 18.6, N 7.5, Rh 18.5. − FAB$^+$-MS: m/z = 561 $[M]^+$, 524 $[M - Cl]^+$, 489 $[M - 2Cl]^+$, 372 $[M - 2Cl - PhCH_2CN]^+$. − IR (selected bands): $\tilde{\nu}$ = 2938 w and 2894 w ν(CH), 2316 m ν(C≡N), 1497 s and 1455 s ν(C=C), 742 s, 730 s and 695 s δ(CH) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 4.17 (s, 2 H) and 4.26 (s, 4 H, CH_2), 7.32−7.40 (m, 15 H, Ph). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.2 (CH_2, 1C), 25.4 (CH_2, 2C), 128.1, 128.6, 129.4 (CH, 2C each) and 128.0, 128.7, 129.5 (CH, 1C each), 127.5 (C_{ipso}, 3C, Ph), 121.9 (1C) and 122.8 (2C) (C≡N). For the toluene solvate $[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5Me$, $C_{27.5}H_{25}Cl_3N_3Rh$ (606.8): calcd. C 54.4, H 4.2, N 6.9; found C 54.9, H 4.4, N 6.6.

***mer*-$[RhCl_3\{PhCH_2C({=}NH)(NH_2)\}_3]$:** A solution of *mer*-$[RhCl_3(PhCH_2CN)_3]$ (0.1 g) in benzyl cyanide (1.0 mL) in an open beaker was placed in a dessicator with 25% aqueous ammonia at the bottom and kept for 1 d at room temperature. After this time diethyl ether (20 mL) was added dropwise with continuous stirring. The precipitate formed was collected on a filter, washed with three portions of Et_2O (each 3 mL) and dried in air at room temperature. Yield: 0.09 g (83%); m.p. 170 °C. − TLC on SiO_2, R_f = 0.36 (eluent $CHCl_3/Me_2CO$ = 3:1, v/v). − $C_{24}H_{30}Cl_3N_6Rh$ (611.8): calcd. C, 47.1, H 4.9, N 13.7, Cl 17.4, Rh 16.8; found C 47.2, H 4.9, N 13.7, Cl 17.3, Rh 16.9. − FAB$^+$-MS: m/z = 612 [M], 575 $[M - Cl]^+$. − IR (selected bands): $\tilde{\nu}$ = 3490 w, 3427 m-w, 3400 m-w, 3329 m-w, 3269 m-w ν(NH), 2921 m-w ν(CH), 1650 vs, br. ν(C=N), 749 s and 702 s δ(CH) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.59 (s, 2 H)

Table 3. Crystal data and structure refinement

	$[RhCl_3(PhCH_2CN)_3]\cdot 1/2\ C_6H_5CH_3$	$[RhCl_3\{PhCH_2C(NH_2){=}NH\}_3]$
Empirical formula	$C_{27.5}H_{25}N_3Cl_3Rh$	$C_{24}H_{30}N_6Cl_3Rh$
Formula weight	606.77	611.80
Temperature, K	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
a, Å	8.3190(4)	31.099(6)
b, Å	13.4682(7)	11.633(2)
c, Å	13.9479(8)	15.344(3)
α (°)	109.481(2)	−
β (°)	105.454(3)	105.91(3)
γ (°)	98.852(3)	−
V(Å^3)	1368.41(12)	5338.4(17)
Z	2	8
$\rho_{calcd.}$ (g/cm^3)	1.473	1.522
μ (Mo) (mm^{-1})	0.938	0.965
Crystal size (mm)	0.1 × 0.08 × 0.08	0.05 × 0.1 × 0.12
θ range for data collection	1.82−26.44	1.88−23.98
Index ranges	$-10 \leq h \leq 0$ $-16 \leq k \leq 16$ $-16 \leq l \leq 17$	$0 \leq h \leq 35$ $0 \leq k \leq 12$ $-17 \leq l \leq 16$
Reflections collected/unique	10079/5608 [$R_{int.}$ = 0.068]	4191/3959 [$R_{int.}$ = 0.048]
Data/restraints/parameters	5608/5/305	3959/0/343
Goodness-of-fit on F^2	1.055	0.999
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0524$, $wR_2 = 0.1243$	$R_1 = 0.0376$, $wR_2 = 0.0739$
R indices (all data)	$R_1 = 0.0793$, $wR_2 = 0.1371$	$R_1 = 0.0596$, $wR_2 = 0.0814$
Largest diff. peak and hole	0.934 and −0.752	0.274 and −0.342

and 3.75 (s, 4 H, CH$_2$Ph), 4.78, 5.00, 5.44 and 5.62 (four s, br, NH$_2$), 7.09 (m, 2 H), 7.23 (m, 4 H) and 7.31 (m, 9 H, Ph), 7.63 (s, br, 3 H, =NH). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 43.3 (3 C, CH$_2$Ph), 127.8 (2 C), 128.1 (1 C), 129.0 (2 C), 129.18 (1 C), 129.22 (1 C), 129.5 (2 C) and 133.8 (3 C, Ph), 170.1 and 171.0 (*C*=NH).

X-ray Crystallography: All crystallographic measurements were carried out with a Nonius Kappa CCD diffractometer equipped with a graphite monochromated Mo-K_α radiation source using θ rotations with 2° frames and a detector-to-crystal distance of 35 mm. The unit cell determination and integration was carried out by the program DENZO-SMN.[47] Data sets were corrected for Lorentz and polarization effects. Structures were solved using heavy-atom methods SHELXL-97.[48] All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in the idealized position and allowed to ride. All crystallographic data and information about refinement of the two structures are given in Table 3 and bond lengths and angles in Table 1 and Table 2.
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-137154 $C_{27.5}H_{25}N_3Cl_3Rh$ and CCDC-137155 $C_{24}H_{30}N_6Cl_3Rh$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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