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The formation of *cis*- and *trans*-[Ru(CN)$_2$(CN^{t}Bu)$_4$] by reductive cleavage of isocyanide ligands; isomer separation by supramolecular interactions with various solvents †

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The octahedral complexes *cis*- and *trans*-[Ru(CN)$_2$(CN^{t}Bu)$_4$] are prepared in quantitative yields from the reaction of $Ru_3(CO)_{12}$ with an excess of the isocyanide and under CO pressure. During the reaction, part of the isocyanide ligands are reductively cleaved to yield the cyanide ligands, isobutene and hydrogen. The latter were unequivocally detected by GC and GC-MS measurements. The complexes are observed in a 1 : 1 mixture of the two isomers. These isomeric coordination compounds may be separated by recrystallization from various solvents. The crystal structures are built up by supramolecular arrangements in which the cyanide ligands act as hydrogen bond acceptors. Therefore the properties of the solvents to act as hydrogen bond donors or acceptors together with the different steric requirements of cyanide ligands arranged in a *cis* or *trans* configuration lead to the crystallization of either the *cis*- or *trans*-isomer or crystalline material containing both isomers, respectively. The use of dichloromethane leads to the precipitaion of crystals with a 1 : 1 mixture of both isomeric complexes. With dry chloroform as the solvent, the *trans*-isomer crystallizes within days, whereas the *cis*-isomer precipitates after months. Using neat chloroform leads to the formation of crystals of the *cis*-isomer only. The use of acetone yields crystals with only the *trans*-isomer present for the dry as well as for the neat solvent.

Introduction

Multinuclear transition metal complexes have received increasing interest during the last decade due to their potential use in electronics or optoelectronics as well as in the field of single-molecule magnets. Compounds in which redox active transition metal centers are arranged linearly by bridging organic ligands have been shown to exhibit properties that allow applications especially in terms of optoelectronic devices.[1] On the other hand, the construction of multinuclear complexes in which the spins of paramagnetic transition metal building blocks add to a high spin multiplicity and which show a strong uniaxial magnetic anisotropy of the molecular compounds show properties of single-molecule magnets.[2]†

Cyanide ligands have quite often been used to link two transition metal fragments. Many compounds have been synthesized from reactions of hexacyanometallates with various paramagnetic transition metal complexes by ligand exchange reactions.[3] Depending on the ligand enviroment of the additional paramagnetic transition metal building blocks not all of the cyanide ligands of the hexacyanometallates may react.

In order to control the architecture of the resulting di- or multinuclear coordination compounds different strategies have been adopted. The use of dinuclear ruthenium compounds with bridging acetate or anilinopyridinate ligands in reactions with other organometallic compounds with a cyanide ligand leads to products with a linear arrangment of the transition metals. The cyanide ligand links the dinuclear ruthenium core with the additional transition metal centers.[4] A triangular arrangment of Fe(III) centers around another Fe(III) complex unit in has been synthesized by the reaction of tris-pyrazolylborato bridged iron complexes with a $[Fe(H_2O)_6]^{3+}$ ion.[5] Various chelating ligands were used to construct starting compounds with either *cis*- or *trans*-geometry of cyanide ligands, which then by reaction with additional paramagnetic building blocks, assemble to give molecular squares or zigzag chains.[6]

Cluster compounds with higher nuclearities may be achieved *e.g.* reacting paramagnetic octacyanometallates with appropriate paramagnetic metal salts. In this way compounds with very high spin multiplicities in the ground state have been observed consisting of $[M_9Mo_6]$ or $[M_9W_6]$ (M = Mn, Ni) cluster cores.[7]

In summary, there is a lack of synthetic procedures that produce coordination compounds of redox-active transition metals with a distinct number of cyanide ligands and with a well defined stereochemistry. In addition, the ligand sphere accompanying the cyanide ligands should be identical for isomeric complexes in order to clearly distinguish between influences of the stereochemistry and electronic properties of additional ligands.

In this report we describe the synthesis of *cis*- and *trans*-[Ru(CN)$_2$(CN^{t}Bu)$_4$] in a quantitative reaction from $Ru_3(CO)_{12}$ and *tert*-butylisocyanide under CO pressure. The two isomeric complexes are easily seperated by either colomn chromatography or by simply by recrystallizing a 1 : 1 mixture of the compounds from the appropriate solvent. The latter will be rationalized by analyzing the architectures of six crystal structures consisting of either the *cis*- or the *trans*-isomer together with various amounts of solvent molecules. This procedures give access to building blocks with two cyanide ligands in *cis*- or *trans*-geometry, in which the additional coordination sphere of the metal remains the same. Thus in the future it will be possible to produce multinuclear aggregates of different shape and to study electronic or magnetic effects without having to take into account the influence of different co-ligands.

Results and discussion

Synthesis and spectroscopic properties of the ruthenium complexes

Treatment of $Ru_3(CO)_{12}$ with an excess of *tert*-butyl isocyanide in toluene and under CO pressure leads to the quantitative formation of a 1 : 1 mixture of *cis*- and *trans*-[Ru(CN)$_2$(CN^{t}Bu)$_4$],

† Electronic supplementary information (ESI) available: Table S1 with selected bond lengths and angles of all compounds, Fig. S1 showing the chains of the *trans*-isomer from neat acetone. See http://www.rsc.org/suppdata/dt/b3/b304199a/

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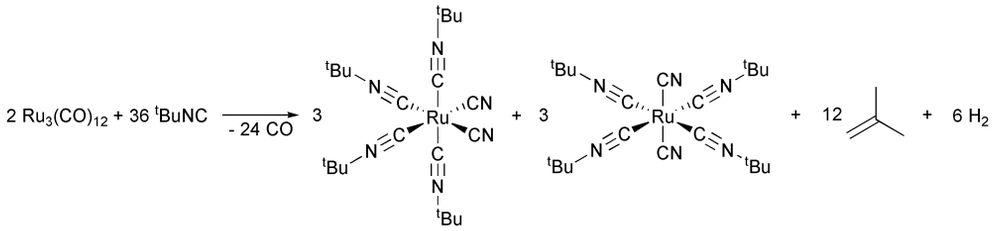

Scheme 1

1 (Scheme 1). Therefore two isocyanide ligands per ruthenium atom have been cleaved during the reaction. Formally the isocyanide is transferred into a cyanide, isobutene and a proton. Since we also detected isobutane from our GC and GC-MS measurements it becomes evident that two protons are reduced to give molecular hydrogen, which hydrogenates isobutene. On the other hand, Ru(0) is oxidized to Ru(II) cations that are observed in the product complexes. Although the standard potential of (Ru/Ru^{2+}) is more positive than $E_0(H_2/H^+)$ the reaction might well proceed due to the high heat of formation of the product complexes.

There are two reaction pathways that would rationalize the formation of the observed reaction products. Pathway 1: the isocyanide is cleaved to give isobutene, a cyanide ion and a proton. Afterwards two protons are reduced to produce molecular hydrogen. The electrons for this process are supplied by the oxidation of a Ru(0) to Ru^{2+} which then is coordinated by the cyanide ions. The hypothetic reverse reaction of this process would be the transition metal induced formation of isocyanide ligands from olefins and cyanide ligands in the presence of an acid. This process has been described in the literature several years ago either from cyanometallates (M = Fe, Ru, Os, Pt) or from hydrocyanic acid in the presence of copper(I) halides.[8]

Pathway 2: Of course one could also think of a homolytic cleavage of the isocyanide to yield a isobutyl radical as well as a $CN^{\bullet}$. The isobutyl radical then would produce isobutene and a hydrogen atom, two of which would form molecular hydrogen. The formal reduction process would be the reduction of $CN^{\bullet}$ to give a cyanide ion. This process seems to be less favourable since it would surely produce $(CN)_2$, which we were not able to detect by GC and GC-MS measurements.

The fact that the reaction only occurs under CO pressure and at elevated temperatures might be understood if the function of CO is the break-up of the trinuclear cluster framework of $Ru_3(CO)_{12}$ producing $Ru(CO)_5$ which is much more reactive.

The IR and NMR spectroscopic properties of *cis*- and *trans*-$[Ru(CN)_2(CN^tBu)_4]$ clearly reflect the different symmetry of the compounds. The isomeric complexes are easily identified by their NMR spectra, in which the *cis*-isomer shows two sets of signals for the isocyanide ligands, whereas the spectra of the *trans*-isomer only show the equivalency of all isocyanide moieties (*cf.* Experimental section).

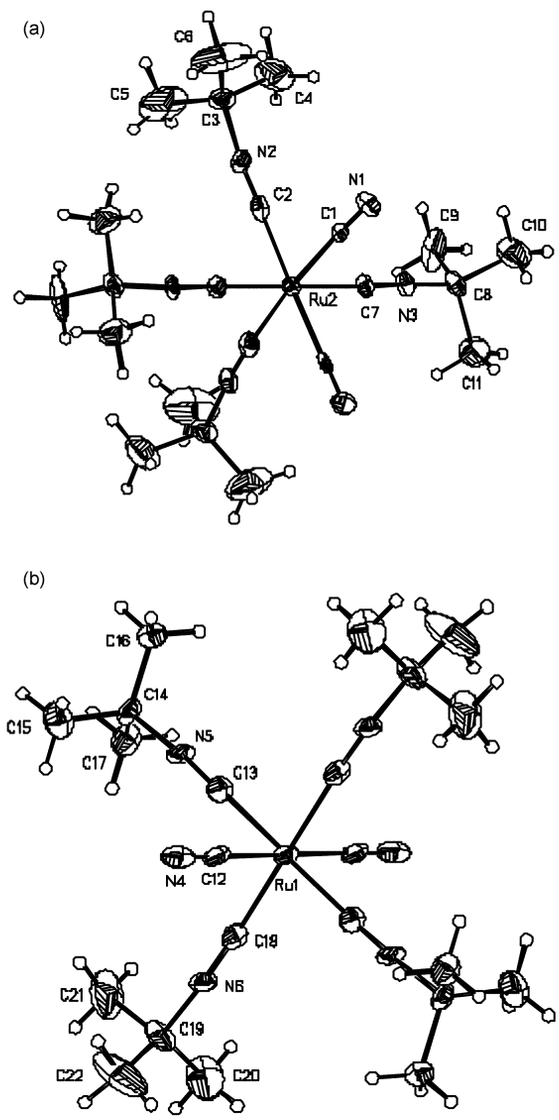

Fig. 1 The molecular structure of *cis*- and *trans*-$[Ru(CN)_2(^tBuNC)_4]$, **1**, from the structural analysis of crystalline *cis*-**1**·*trans*-**1**·$4CH_2Cl_2$.

Structure determinations

Recrystallization of *cis*- and *trans*-$[Ru(CN)_2(CN^tBu)_4]$ from different solvents leads to the crystallization of solvates of one of the isomeric complexes. Only in the case of dichloromethane as the solvent are crystals consisting of both isomers obtained. Selected bond lengths and angles of the coordination compounds may be found in the ESI.† Fig. 1 shows the molecular structure of both the *cis*- and *trans*-isomer from the structure determination of the crystals from dichloromethane.

There are two structure determinations in which the *cis*-isomer has been observed and four with the *trans*-isomer present in the crystal structure. As expected, there are no significant differences in the molecular structures if the *cis*- and *trans*-complexes are crystallized from different solvents. In all cases the ruthenium atoms are octahedrally surrounded by the six ligands. The carbon ruthenium bond lengths of the cyanide ligands are about 5–6 pm longer than the corresponding bonds of the isocyanide ligands, which is due to the better π-back-bonding ability of the isocyanides compared to cyanide ligands. In all crystal structures except the dichloromethane solvate one or two *tert*-butyl groups are statistically disordered. The occupation factors lie in a range of 60 : 40 to 70 : 30 percent and thus the models with the lower probabilities were refined isotropically.

There are only a few structurally characterized complexes of a group 8 metal with four isocyanide and two additional anionic ligands. The anionic ligands are either halides,[9] thiolates[10] or azide.[11] Interestingly, the latter compound was crystallized as a thiourea complex. In all cases the complexes show a *trans*-configuration. In addition, two structure analyses of

Table 1 Hydrogen bond distances (pm) and angles (°) of the different solvates of *cis*- and *trans*-[Ru(CN)$_2$(CNtBu)$_4$], **1**

Compound	X–H ··· Y	H ··· Y	X ··· Y	C–H–Y
cis-**1**·2CH$_2$Cl$_2$	C–H ··· N	250.9	338.9	150.9
		277.5	356.2	138.7
	C–H ··· Cl	297.5	389.8	161.9
		317.0	399.9	130.7
		318.5	386.6	150.9
cis-**1**·CHCl$_3$·2H$_2$O	O–H ··· O	–	275.8	–
		–	279.8	–
	O–H ··· N	–	289.7	–
		–	297.9	–
	C–H ··· O	236.3	329.9	159.4
	C–H ··· N	217.0	314.6	164.9
	C–H ··· Cl	290.9	365.9	134.0
		305.4	386.6	141.2
		310.1	403.5	159.7
		312.1	393.0	140.8
cis-**1**·3CHCl$_3$	C–H ··· N	214.5	313.4	170.0
		222.3	320.9	168.3
		231.5	329.1	165.1
	C–H ··· Cl	288.7	349.6	121.1
		293.8	375.4	141.7
		294.0	346.4	114.6
		298.8	346.1	111.2
		300.4	359.3	119.8
		302.1	396.6	161.5
		310.4	378.4	127.8
		311.0	399.7	151.2
		312.7	388.5	135.4
trans-**1**·2CH$_2$Cl$_2$	C–H ··· N	237.3	331.5	163.7
		241.5	336.8	167.2
	C–H ··· Cl	295.3	389.5	148.0
		309.9	394.6	167.2
trans-**1**·2CHCl$_3$	C–H ··· N	226.2	318.6	164.0
	C–H ··· Cl	300.5	390.7	153.6
		312.0	403.4	155.9
trans-**1**·0.5Me$_2$CO	C–H ··· N	264.9	346.2	140.6
	C–H ··· O	263.3	299.5	102.1
		268.8	299.5	98.6
trans-**1**·0.75Me$_2$CO·0.75H$_2$O	C–H ··· N	251.4	344.2	158.1
		265.9	359.9	161.0
		267.7	332.0	123.6
	C–H ··· O	266.4	349.3	125.1
		273.7	370.0	167.5

[Fe(CN)$_2$(MeNC)$_4$] were published, one of which is a solvate with two molecules of chloroform per complex unit.[12] These structurally characterized compounds both show a *cis*-configuration of the coordination compounds.

The crystal structures of all solvates of **1** are determined by the properties of the complex units and the solvents to act as hydrogen bond donors and acceptors. Table 1 shows the bond lengths and angles of the hydrogen bonds present in the crystal structures that were determined in this investigation.

In all cases the cyanide ligands act as acceptors of strong hydrogen bonds. In the case of halogenated solvents also the chlorine atoms act as hydrogen bond acceptors. Hydrogen bond donors are the methyl groups of the isocyanide ligands or acetone, repsectively, as well as the hydrogen atoms of dichloromethane or chloroform.

Recrystallization of a 1 : 1 mixture of *cis*- and *trans*-[Ru(CN)$_2$(CN^{t}Bu)$_4$] from dichloromethane leads to the formation of crystals containing both isomers as well as two molecules of the solvent per complex unit. The ruthenium atom of the *trans*-isomer is situated on a crystallographic center of inversion. The ruthenium atom of the *cis*-isomer is observed on a crystallographic two-fold axis. The crystal structure is built up by seperate infinite chains of the *cis*-isomer and additional infinite chains of the *trans*-isomer. Fig. 2 shows the chain of the

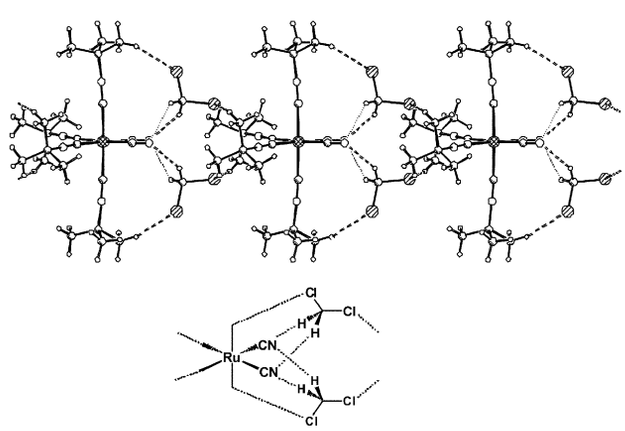

Fig. 2 The crystal structure of *cis*-**1**·2CH$_2$Cl$_2$ (co-crystallizes with *trans*-**1**·2CH$_2$Cl$_2$, *cf.* Fig. 3).

cis-complex, in which each molecule of dichloromethane is connected to one molecule of the ruthenium complex *via* two C–H ··· N interactions. Therefore, each cyanide nitrogen atom interacts with both solvent molecules *via* one strong and another less strong hydrogen bond showing a bifurcated hydrogen

binding arrangement. In addition, each molecule of dichloromethane is interacting with one of the isocyanide ligands *via* a C–H · · · Cl hydrogen bond. These adducts of one complex fragment and two solvent molecules are interconnected to produce infinite chains by C–H · · · Cl hydrogen bonds between the remaining chlorine atom and the *tert*-butyl groups of a neighboring complex molecule.

Fig. 3 shows the infinite chains built up up by two molecules dichloromethane per molecule of the *trans*-isomer of the ruthenium complex compound. Again both hydrogen and both chlorine atoms of the solvent molecules are engaged in the hydrogen bonding interactions. In analogy to the *cis*-isomer the cyanide ligands of the *trans*-isomer also show bifurcated hydrogen bonds to two solvent molecules. The second hydrogen atom of each molecule of dichloromethane interacts with the cyanide ligand of the next complex unit. The two chlorine atoms per solvent molecule are also interacting with different molecules of the ruthenium compound. In contrast to the structure of the *cis*-isomer the supramolecular arrangement of the *trans*-isomer is already built up by the strong C–H · · · N interactions.

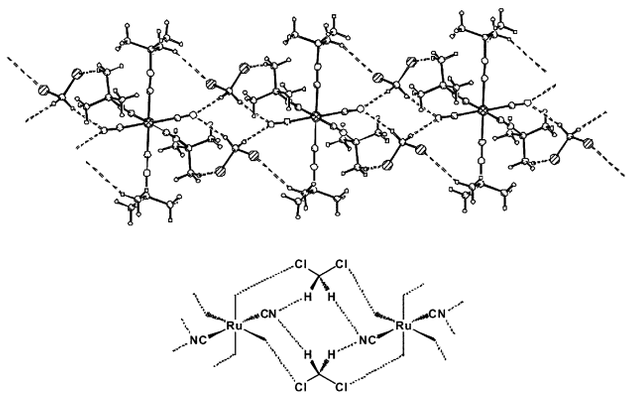

Fig. 3 The crystal structure of *trans*-**1**·2CH_2Cl_2 (co-crystallizes with *cis*-**1**·2CH_2Cl_2, *cf.* Fig. 2).

Thus dichloromethane is capable of efficiently interacting with complexes with cyanide ligands, which always act as hydrogen bond acceptor sites, both in a *cis*- and *trans*-configuration. This is possible because dichloromethane itself exhibits two potential hydrogen bond donor and hydrogen bond acceptor groups and thus is flexible enough to build up supramolecular arrangements with complexes of different steric requirements.

Changing the solvent from dichloromethane to dry chloroform leads to a decrease of potential hydrogen bond donor sites in the solvent molecules but to an increase of acceptor sites. Crystallization of a 1 : 1 mixture of both isomeric complexes thus leads to the precipitation of crystals which only consist of the *trans*-isomer within days. In addition, two chloroform molecules per complex molecule are present. The ruthenium atom again is situated on a crystallographic center of inversion. The crystal structure is shown in Fig. 4. As expected, the proton of the solvent molecule forms a strong hydrogen bond towards the most efficient hydrogen bond acceptor sites which are the cyanide ligands. The aggregates of one complex molecule and two solvent molecules are interconnected to infinite planes, because each solvent molecule establishs hydrogen bond contacts to two different neighboring ruthenium complexes by C–H · · · Cl interactions.

If the chloroform solution from which the *trans*-isomer crystallized is kept at room temperature a very slow precipitation of differently shaped crystals starts after about three weeks leading to crystals suitable for X-ray diffraction after two months. These crystals consist of the *cis*-isomer also as a chloroform solvate. In this case three solvent molecules per complex unit are observed. Fig. 5 shows the crystal structure of this

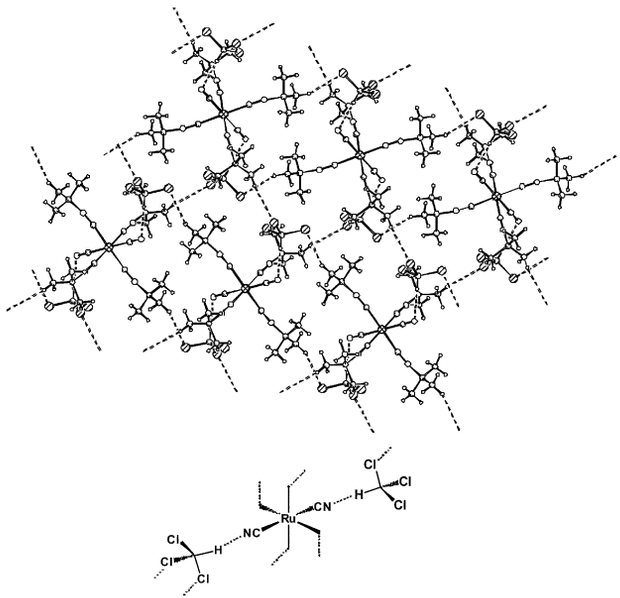

Fig. 4 The crystal structure of *trans*-**1**·2$CHCl_3$.

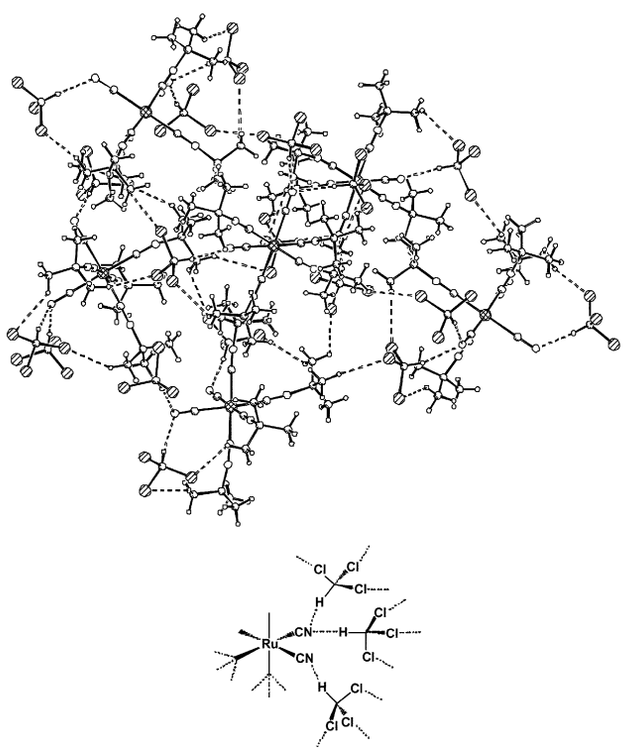

Fig. 5 The crystal structure of *cis*-**1**·3$CHCl_3$.

aggregates. Two molecule of chloroform are connected to one of the cyanide ligands by C–H · · · N interactions. The second cyanide is connected only to one chloroform. A very complicated three-dimensional network is built up by nine different C–H · · · Cl hydrogen bonds of isocyanide ligands towards the chlorine atoms of the solvent molecules.

The most interesting observation that we made is the fact that by just adding small portions of water to the same solvent chloroform leads to a complete change of selectivity during the crystallization process. Using neat chloroform leads to the precipitation of crystals of pure *cis*-[$Ru(CN)_2(CN^tBu)_4$] from a 1 : 1 mixture of both isomers. The crystal structure of the *cis*-isomer from neat chloroform is shown in Fig. 6. It becomes evident, that the crystallization of the *cis*-isomer is due to the incorporation of two additional water molecules into the crystal structure together with the ruthenium complex and one

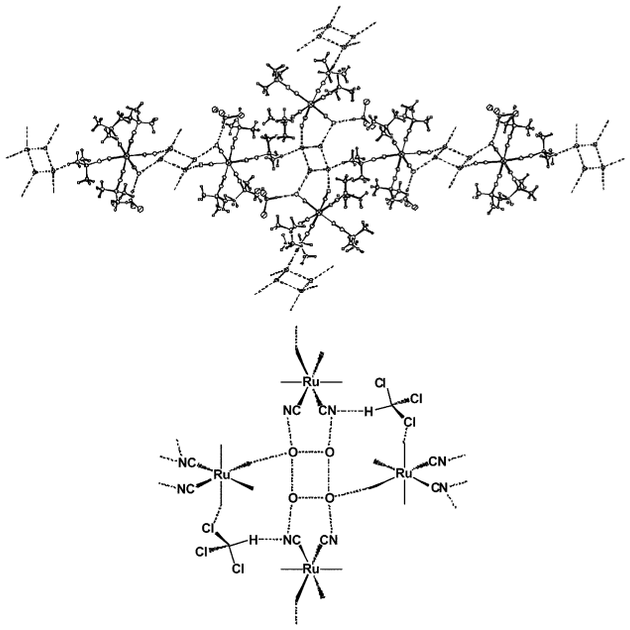

Fig. 6 The crystal structure of *cis*-**1**·$CHCl_3$·$2H_2O$.

solvent molecule per complex. The hydrogen atoms of the water molecules were not localizable from difference Fourier maps, but the alignment of hydrogen bonds is nevertheless obvious. Four water molecules form a rectangle by four strong hydrogen bonds. These water rectangles show O–H ··· N hydrogen bond interactions to two complex molecules and two additional C–H ··· O contacts to another two coordination compounds, thus establishing an infinite plane. One of the two cyanide ligands additionally interacts with the hydrogen atom of the chloroform molecule. The chlorine atoms also take part in the hydrogen bond network by rather weak C–H ··· Cl hydrogen bonds towards *tert*-butyl groups again. These interactions have been omitted in Fig. 6 for clarity but they are detailed in Table 1.

The chloroform solvate of *cis*-$[Fe(CN)_2(MeNC)_4]$ is also built up by hydrogen bond interactions between the solvent and the cyanide ligands as hydrogen bond acceptors and methyl groups of the isocyanide ligands as hydrogen bond donors.[12b] Each cyanide binds one molecule of chloroform. Only one of the chlorine atoms of chloroform is involved in the hydrogen bond network.

In additional experiments we wanted to use non-halogenated solvents in order to exclude the C–H ··· Cl interactions in the construction of the hydrogen bond networks. So we used acetone to recrystallize 1 : 1 mixtures of the two isomeric coordination compounds. From dry as well as from neat acetone only the *trans*-isomer crystallizes. The supramolecular structure is of course slightly diferent due to the incorporation of water in the latter case.

Fig. 7 shows the crystal structure of the solvate of the *trans*-isomer with acetone. The ruthenium atom again is observed on a crystallographic center of inversion. Infinite chains are built up by C–H ··· N interactions between the cyanide ligands and *tert*-butyl groups of neighboring complex units. The acetone ligands are only interacting at the periphery of these chains by quite weak hydrogen bonds of the carbonyl oxygen atom towards *tert*-butyl groups of the isocyanide ligands. The finding that these solvent molecules are just weakly bound is also expressed by the fact that they occupy statistically only half of the positions in the crystal lattice.

If neat acetone is used as the solvent the *trans*-isomer crystallizes with one molecule of acetone and one molecule of water per complex unit. One of the complexes is found at a special position again whereas the other is observed at a general position. These different complexes form two discrete kinds of

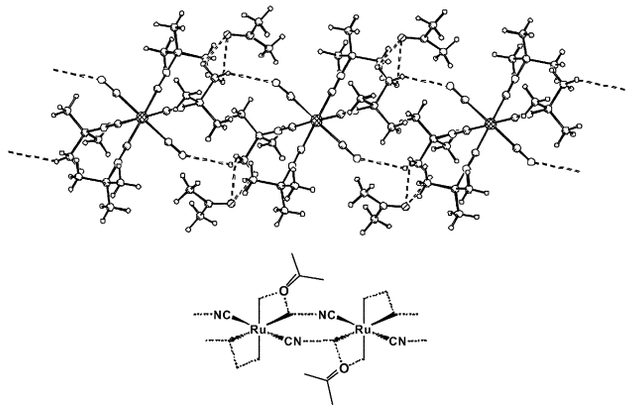

Fig. 7 The crystal structure of *trans*-**1**·$0.5Me_2CO$.

infinite chains built up by hydrogen bonds. Both chains consist of the *trans*-isomer but in one only acetone is present as the solvating molecule whereas the other chain is exclusively built up by water molecules as the solvent. The infinite chain with acetone present is only slightly different from that resulting from recrystallization from dry acetone (Fig. S1, ESI †). Again the chain is built up by C–H ··· N interactions between the ruthenium complexes themselves. Acetone is bound in the periphery of the chain, but it is bound more tightly by additional C–H ··· N hydrogen bonding towards cyanide groups.

The infinite chains built up by the *trans*-complex with water is shown in Fig. 8. In this case the ruthenium atom again is situated on a crystallographic center of inversion. The incorporation of water as the better hydrogen bond donor compared to methyl groups leads to chains in which the molecules are connected by one O–H ··· N hydrogen bond from water towards a cyanide ligand as well as one C–H ··· O contact from one of the methyl groups towards water.

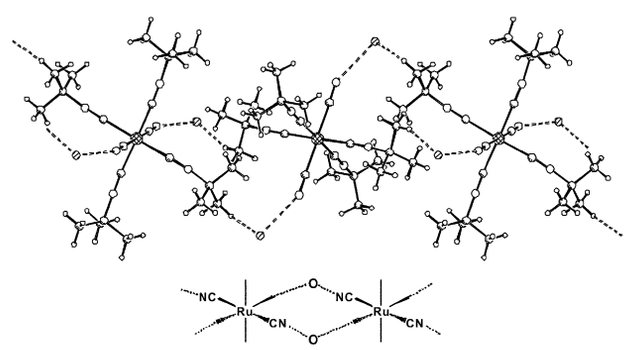

Fig. 8 The crystal structure of *trans*-**1**·$0.75H_2O$ (co-crystallizes with *trans*-**1**·$0.75Me_2CO$, *cf.* Fig. S1, ESI †).

In general, the bond lengths and angles that we observed for the hydrogen bond interactions in the crystal structures of the different solvates of *cis*- or *trans*-$[Ru(CN)_2(^tBuNC)_4]$ and which are summarized in Table 1, fit very well to corresponding values reported in the literature. This is not only true for the very strong O–H ··· O and O–H ··· N interactions that we found for the structure of *cis*-**1**·$CHCl_3$·$2H_2O$ but also for the quite weak hydrogen bonds with a C–H donor site.[13] It is also obvious that the C–H ··· O and C–H ··· N interactions tend to linearity in most cases. Still one has to keep in mind that these hydrogen bonds are weak and so other effects in the crystal packing may have a distinct influence on the C–H ··· X angles, which thus show a quite broad distribution.[13d,14] On the other hand, the C–H ··· Cl angles that we observed mostly lie in a range of 110–140°. This is in agreement with database researches which also showed the acceptor directionality to have a maximum at *ca.* 100–120°.[15] This was interpretated in terms of the higher basicity of the p-type lone-pair at chlorine

Table 2 Crystal and intensity data for **1** from different solvents

Compound	*cis*-**1** and *trans*-**1**·4CH_2Cl_2	*trans*-**1**·2$CHCl_3$	*cis*-**1**·3$CHCl_3$	*cis*-**1**·$CHCl_3$·2H_2O	*trans*-**1**·0.5Me_2CO	*trans*-**1**·0.75Me_2CO·0.75H_2O
Formula	$C_{22}H_{36}N_6Ru$·2CH_2Cl_2	$C_{22}H_{36}N_6Ru$·2$CHCl_3$	$C_{22}H_{36}N_6Ru$·2$CHCl_3$	$C_{22}H_{36}N_6Ru$·$CHCl_3$·2H_2O	$C_{22}H_{36}N_6Ru$·0.5C_3H_6O	$C_{22}H_{36}N_6Ru$·0.75C_3H_6O·0.75H_2O
M_r	655.49	724.38	843.74	639.01	514.68	662.99
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
T/K	183	183	183	183	183	183
Crystal color	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal size	0.5 × 0.3 × 0.3	0.3 × 0.3 × 0.25	0.4 × 0.3 × 0.3	0.5 × 0.1 × 0.05	0.5 × 0.3 × 0.3	0.2 × 0.2 × 0.1
a/Å	34.673(7)	10.2282(4)	17.3118(4)	16.909(3)	10.3896(3)	26.9630(7)
b/Å	10.085(1)	10.0166(4)	17.9529(5)	18.285(4)	9.6085(3)	9.4494(2)
c/Å	19.288(2)	17.6631(5)	26.2415(5)	22.197(4)	14.8321(5)	18.3389(4)
α/°	90	90	90	90	90	90
β/°	92.205(8)	104.759(3)	90	90	91.64(2)	100.905(2)
γ/°	90	90	90	90	90	90
V/Å^3	6740(2)	1749.9(1)	8155.8(3)	6863(2)	1480.06(8)	4588.1(2)
Z	8	2	8	8	2	6
F(000)	2704	740	3424	2624	540	1684
D_c/g cm^{-3}	1.292	1.375	1.374	1.233	1.155	1.162
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	*Pbca*	*Pbca*	*P*2/*n*	*P*2/*c*
μ/mm^{-1}	0.797	0.929	0.998	0.716	0.550	0.536
θ limit/°	2.34 < θ < 27.35	2.92 < θ < 27.44	1.55 < θ < 27.47	1.88 < θ < 27.47	2.12 < θ < 27.44	1.54 < θ < 27.46
Scan mode	ω-Scan, ϕ-scan	ω-Scan, ϕ-scan	ω-Scan, ϕ-scan	ω-Scan, ϕ-scan	ω-Scan, ϕ-scan	ω-Scan, ϕ-scan
Reflections measured	2288	6727	17214	14031	5908	16849
Independent reflections	1974	3914	9298	7642	3370	10277
R_{int}	0.0194	0.0251	0.0777	0.1523	0.0182	0.0401
Reflections observed ($F_o^2 > 2\sigma(F_o^2)$)	1797	3173	4718	3209	2780	7341
No. of parameters	318	197	415	349	174	498
Goodness-of-fit	1.075	1.092	1.045	0.973	0.921	1.053
R_1	0.0348	0.0308	0.0618	0.0547	0.0401	0.0507
wR_2	0.0853	0.0676	0.1527	0.0927	0.1131	0.1124
$\Delta\rho_{max}$/e Å^{-3}	0.311	0.486	0.673	0.298	0.991	1.189

which is perpendicular to the less basic sp-type lone-pair situated opposite with respect to the C–Cl bond in the solvent molecules themselves.[16]

Investigations on the question, whether the reductive cleavage of isocyanides to produce transition metal complexes with a defined number of cyanide ligands from metal carbonyl compounds is a general reaction principle, are ongoing at the moment. We are also trying to combine the ruthenium complexes described herein as building blocks for heteronuclear assemblies of organometallic moieties in order to explore their magnetic and optical properties.

Experimental

General

Infrared spectra were recorded on a Perkin Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz, ^{13}C: 50.32 MHz, $CDCl_3$ as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. GC spectra were aquired from a gas chromatograph Chrompack CP 9000 instrument using He as the mobile phase.

X-Ray crystallographic study

The structure determinations were carried out on an Enraf Nonius Kappa CCD diffractometer, crystal detector distance 29 mm, using graphite-monochromated Mo-Kα radiation. The crystal was mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS86 and SHELXL93.[17] Computation of the structures was acomplished with the program XPMA[18] and molecular illustrations drawn using the program XP.[19] The crystal and intensity data are given in the ESI.†

CCDC reference numbers 208499 (*cis*- and *trans*-**1**·4CH_2Cl_2), 208500 (*trans*-**1**·2$CHCl_3$), 208501 (*cis*-**1**·3$CHCl_3$), 208502 (*cis*-**1**·$CHCl_3$·2H_2O), 208503 (*trans*-**1**·0.5Me_2CO) and 208504 (*trans*-**1**·0.75Me_2CO·0.75H_2O).

See http://www.rsc.org/suppdata/dt/b3/b304199a/ for crystallographic data in CIF or other electronic format.

Experimental procedures

A 50 mL autoclave charged with $Ru_3(CO)_{12}$ (65 mg, 0.10 mmol), *tert*-butylisocyanide (0.8 mL, 7.7 mmol) and toluene (5 mL) was pressurized with carbon monoxide (10 bar) and heated at 145 °C over night. After cooling all volatailes were removed *in vacuo*. NMR spectra of the crude reaction mixture reveal the quantitative course of the reaction. Recrystallization of the remaining solid using mixtures of dichloromethane and light petroleum (bp 40–60 °C) afforded the solvated isocyanide complex in two isomeric forms (165 mg, 0.25 mmol, 83%). X-Ray quality crystals were obtained by slow diffusion of either heptane or diethyl ether in a dichloromethane, chloroform or acetone solution of the isocyanide complex using a diffusion tube. Separation of the two isomers was achieved either by recrystallization from dry (*trans*-isomer) or neat (*cis*-isomer) chloroform or chromathography on silica using aceton as the eluent. $C_{22}H_{36}N_6Ru$·1.5$CHCl_3$ (M = 664.7), calc.: C 42.46, H 5.69, N 12.64, found: C 42.15, H 6.10, N 12.75%. FAB MS, *m*/*z* (ion, %): 487 (M^+, 37); 460 (M^+ − HCN, 10); 433 (M^+ − C_4H_8, 33); 404 (M^+ − Me_3NC, 8); 375 (M^+ − 2C_4H_8, 25); 348 (M^+ − Me_3NC − C_4H_8, 20); 319 (M^+ − 3C_4H_8, 33); 292 (M^+ − Me_3NC − 2C_4H_8, 44); 263 (M^+ − 4C_4H_8, 45); 236 (M^+ − ^{t}BuNC − 3C_4H_8, 100); 209 (M^+ − 2Me_3NC − C_4H_8, 52).

trans-Isomer: IR, KBr disk, ν/cm^{-1}: 2982m, 2926m, 2150vs, 2108m, 1459m, 1372m, 1237w, 1202s, 571w, 554m, 481w, 433w. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 1.47 (s, Me_3CNC). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 30.62 (Me_3CNC), 57.12 (Me_3CNC), 136.43 (CN), 143.01 (br, Me_3CNC).

cis-Isomer: IR, KBr disk, ν/cm^{-1}: 2982m, 2938w, 2214m, 2156vs, 2118s, 1460m, 1400m, 1372s, 1236m, 1201s, 562m, 550m, 481w, 450w, 433w. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 1.42 (s, Me_3CNC), 1.44 (s, Me_3CNC). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 293 K): δ 30.46 (Me_3CNC), 30.62 (Me_3CNC), 56.88 (Me_3CNC), 57.07 (Me_3CNC), 134.99 (CN), 142.56 (br, Me_3CNC), 144.01 (br, Me_3CNC).

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