

The reaction of manganese carbonyl with *tert*-butylisocyanide: Synthesis and characterization of *cis*- and *trans*-[Mn^I(^tBuNC)₄(CN)(CO)]

Kathi Halbauer, Helmar Görls, Tamara Fidler, Wolfgang Imhof *

Friedrich-Schiller-University, Institute of Inorganic and Analytical Chemistry, Lessingstr. 8, 07743 Jena, Germany

Received 2 June 2006; received in revised form 21 December 2006; accepted 22 December 2006

Available online 18 January 2007

Abstract

The reaction of Mn₂(CO)₁₀ with *tert*-butyl isocyanide in the presence of 10 bar of carbon monoxide leads to the formation of *cis*- and *trans*-[Mn(^tBuNC)₄(CN)(CO)], **1a** and **1b**, in good yields together with [Mn(^tBuNC)₆]CN (**2**), as a minor product. Nevertheless, the reaction pathway highly depends on the reaction conditions. An interesting side-product is obtained, if chloroform is used during the workup procedure. Compound **3** is composed of cationic [Mn(^tBuNC)₅(CO)] units as well as dinuclear anionic [Mn(^tBuNC)₄(CO)(μ-CN)MnCl₃] moieties. If no additional CO pressure is applied to the system, the organic product *N,N'*-di-*tert*-butyl-3,5-bis-*tert*-butylimino-4-phenylcyclopent-1-ene-1,2-diamine (**4**), is formed in considerable amount. Compound **4** most probably is produced via a double benzylic C–H activation of the solvent toluene and the oligomerization of four isocyanide moieties. The reaction of **1b** with Co(NO₃)₂ leads to the isolation of the trinuclear cyanide bridged coordination compound {[Mn(^tBuNC)₄(CO)(μ-CN)₂Co(NO₃)₂], **5**, in which the cobalt atoms are tetrahedrally surrounded by the two cyanide ligands and the η¹-coordinated nitro groups. In contrast to the reaction of **1b**, treatment of the dicyano complexes *cis*- or *trans*-[Ru(^tBuNC)₄(CN)₂] with Co(NO₃)₂ results in the formation of the coordination polymers {[Ru(^tBuNC)₄(CN)₂]Co(NO₃)₂]_n, **7** (*trans*) and **9** (*cis*). All new compounds are characterized by X-ray diffraction experiments. © 2007 Elsevier B.V. All rights reserved.

Keywords: Manganese; Isocyanide ligands; Cyanide ligands; Coordination polymers; X-ray

1. Introduction

The synthesis of cyanide bridged coordination polymers has found considerable interest corresponding to the possibilities of tuning the electronic and/or magnetic coupling between the bridged metal centers [1]. It has been pointed out that the magnetic properties of such a supramolecular aggregate is dependent on the nature of the transition metals and their oxidation state as well as on the number and the relative arrangement of the metal centers with respect to each other. The latter prerequisites often are difficult to control if homoleptic cyanometallates are introduced in the formation of coordination polymers. Thus starting compounds with a limited number of cyanide ligands in a

well-defined stereochemistry might be ideal starting compounds for this kind of investigations.

Some of us recently found that the reaction of ruthenium carbonyl with *tert*-butylisocyanide under CO pressure produces the octahedral ruthenium complexes [Ru(^tBuNC)₄(CN)₂] as a mixture of the *cis*- and *trans*-isomers in quantitative yield [2]. Slight modifications of the reaction conditions allow the synthesis of the corresponding iron(II) derivatives from Fe₂(CO)₉ [3]. The ruthenium complexes have already been introduced to the formation of cyanide bridged coordination polymers. These reactions demonstrated that the arrangement of metal centers relative to each other can be controlled by the use of the isomeric *cis*- or *trans*-complexes, respectively, and that the different isomeric coordination polymers show distinctively different magnetic properties [4]. Nevertheless, cyano complexes of paramagnetic transition metals like e.g. Mn²⁺ would be much more interesting starting compounds for

* Corresponding author. Tel.: +49 3641 948 185; fax: +49 3641 948 102.
E-mail address: Wolfgang.Imhof@uni-jena.de (W. Imhof).

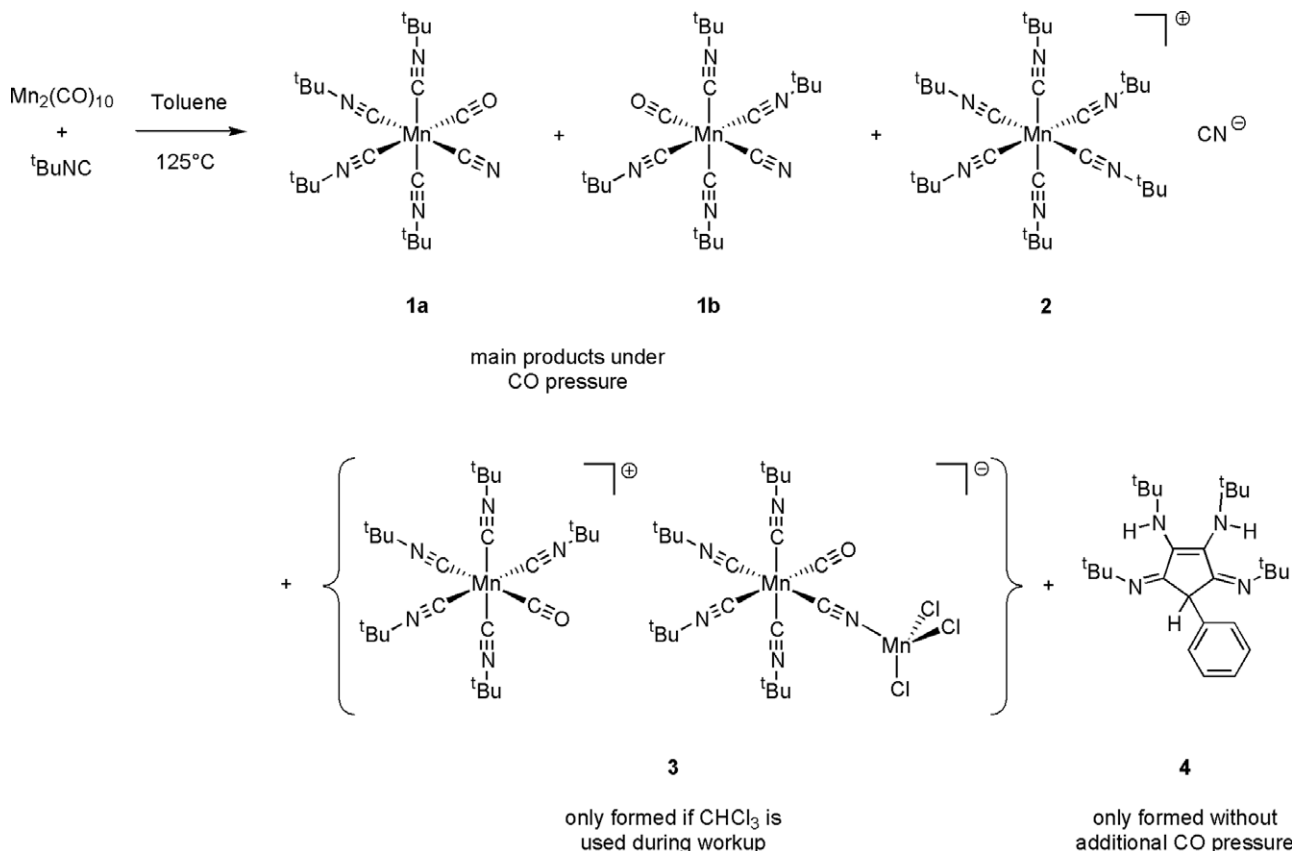
the synthesis of cyanide bridged coordination polymers. The results of the reaction of $\text{Mn}_2(\text{CO})_{10}$ with *tert*-butylisocyanide under various reaction conditions are described in this report.

2. Results and discussion

The reaction of $\text{Mn}_2(\text{CO})_{10}$ with *tert*-butylisocyanide proceeds via the oxidation of the transition metal and the concomitant reductive cleavage of the isocyanide in analogy to iron and ruthenium carbonyl compounds [2,3]. The isolated products are depicted in Scheme 1. In the reaction of $\text{Ru}_3(\text{CO})_{12}$ we recognized that moderate CO pressure was necessary to stabilize mononuclear metal carbonyl fragments. Our first experiments with $\text{Mn}_2(\text{CO})_{10}$ were therefore also performed under 10 bar of carbon monoxide. This leads to the isolation of the mononuclear compounds *cis*- and *trans*- $[\text{Mn}(\text{tBuNC})_4(\text{CN})(\text{CO})]$ (**1a** and **1b**), in excellent yields. So starting from $\text{Mn}_2(\text{CO})_{10}$ the metal atom is only oxidized to the +1-state and not to the +2-state as it was observed for the corresponding reaction of ruthenium and iron carbonyl compounds [2,3]. The IR- and MS-data, the elemental analysis (cf. Experimental Part) as well as the outcome of the X-ray structure analysis unequivocally show that **1a** and **1b** are not the originally expected compound $[\text{Mn}(\text{tBuNC})_4(\text{CN})_2]$. The IR-spectrum of **1a** and **1b** exhibits two sets of bands representing

the carbon monoxide ligand (app. 1900 cm^{-1}) as well as the cyanide and isocyanide groups (app. 2100 cm^{-1}).

The molecular structure of **1b** is presented in Fig. 1, the most important bond lengths and angles are summarized in Table 1. The manganese atom is octahedrally coordinated by four isocyanide ligands, one carbon monoxide group and one cyanide ligand, the latter showing a *trans*-arrangement. Although nitrogen and oxygen are not reliably distinguishable by X-ray crystallography, the different metal carbon bond lengths (Mn–C21 $199.7(3)\text{ pm}$, Mn–C22 $180.3(3)\text{ pm}$) allow the localization of the CO and CN ligand, respectively. In agreement with earlier studies on mixed carbonyl cyanide transition metal complexes the shorter metal carbon bond length is typical for the carbon monoxide ligand [5]. In addition, the supramolecular structure of **1b** (Fig. 2) is also indicative of our assignment. **1b** crystallizes with one molecule of water per asymmetric unit. The solvent molecule is engaged in several hydrogen bond interactions. As it would be expected the strongest hydrogen bonds are observed between the water molecules and the negatively charged cyanide ligands. These interactions lead to the formation of a cyclic aggregate consisting of two water molecules and two complex units (Fig. 2). The three dimensional crystal structure finally is built up by additional weak C–H \cdots O interactions of *tert*-butyl substituents towards the water molecule or the CO ligand. The same central cyclic motif has been structurally character-



Scheme 1.

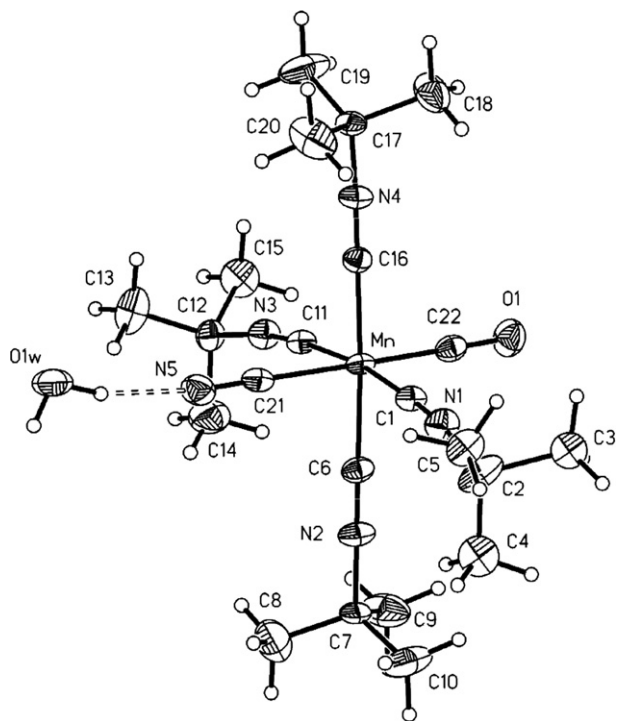


Fig. 1. Molecular structure of **1b**. Displacement parameters are drawn at the 45% probability level.

ized only four times before [6]. A more general statistic on hydrogen bonds between metal bound cyanide ligands and water or alcohol solvent molecules on the basis of 285 structure analyses shows that the hydrogen bond distances of 291.2 pm and 297.6 pm, respectively, observed in the crystal structure of **1b** are slightly longer than the average (*cf.* Supplementary Material) [7]. The hydrogen bond distances between the CO ligand and the hydrogen atoms of hydrocarbon substituents are also in the range that is typically observed for this kind of interaction [8].

Together with **1a** and **1b** compound **2** is produced in low yields. In contrast to **1a** and **1b** the IR spectrum of **2** shows no signals representing carbon monoxide ligands. The same is true for the ^{13}C NMR spectrum. The composition of **2** as a manganese(I) complex octahedrally surrounded by six isocyanide ligands is unequivocally demonstrated by the mass spectrum in which a peak for $[\text{Mn}(\text{tBuNC})_6]^+$ is observed. Similar compounds which only differ in the counterion have already been described in the literature and show analogous spectroscopic and redox properties [9].

Since our goal was to prepare Mn(II) coordination compounds with cyanide ligands in a well-defined stereochemistry, we looked at the redox behaviour of the compounds **1b**, **2** and **5** by CV measurements, the latter being a trinuclear compound in which two manganese(I) complex units are bridged by a cobalt atom via the cyanide ligands of **1b** (*vide supra*). The outcome of the experiments is depicted in Fig. 3 and shows that the manganese centers may be quasi-reversibly oxidised at half-wave potentials of 0.109 (**1b**), 0.0305 (**2**) and 0.205 (**5**) V vs. ferrocene. The plot of the

redox behaviour of **5** quite likely represents two very similar one electron oxidation steps corresponding to the oxidation of the two manganese(I) centers which means that the communication between the two manganese atoms over the cyanide bridges and the central cobalt atom obviously is quite weak.

If chloroform is used during the workup procedure of the reaction mixture another interesting side-product is obtained in very small yields. Compound **3** is an ionic compound with both the cation and the anion being manganese complex units. The IR-spectrum again shows bands typical for the stretching frequencies of cyanide and isocyanide as well as of CO ligands (2178 , 2115 , 2070 cm^{-1} and 1949 , 1927 cm^{-1}). The molecular structure of the cation with the general formula $[\text{Mn}(\text{tBuNC})_5(\text{CO})]^+$ is shown in Fig. 4, bond lengths and angles are presented in Table 1. It consists of an octahedrally coordinated Mn^+ ion surrounded by five *tert*-butyl isocyanide and one carbon monoxide ligand. The metal carbon bond length of the CO group again is significantly shorter than the average Mn–C bond length towards the isocyanide moieties ($182.9(4)$ vs. $191.8(3)$ pm). As it is expected the manganese carbon bond length in *trans*-position with respect to the carbon monoxide ligand is the longest manganese isocyanide bond. The molecular structure of the anion of **3** with the general formula $[\text{Mn}(\text{tBuNC})_4(\text{CO})(\mu\text{-CN})\text{MnCl}_3]^-$ is depicted in Fig. 5. The anion is a dinuclear species consisting of the *cis*-isomer of **1a** together with an additional $[\text{MnCl}_3]^-$ unit. The short manganese carbon bond length Mn1–C1 of $182.7(4)$ compared to the other metal carbon bond lengths in the anion again allows the assignment of this ligand as a CO ligand. The metal carbon bond length of the cyanide ligand ($197.2(3)$ pm) is elongated compared to the corresponding bond in **1b** because of the function of this cyanide moiety acting as a bridging ligand towards Mn2. In contrast to Mn1 and Mn3 showing an oxidation state of +1, Mn2 has to be assigned an oxidation state of +2 so that all charges in **3** add up to zero. Searching the Cambridge Structural Data Base [7] for compounds in which a manganese atom with at least one CO and one cyanide ligand in its coordination sphere bridged to another metal *via* the cyanide ligand yields 34 hits. Just one of them is a structurally characterized compound highly related to **3** showing an MnCl_3 moiety attached to a bridging cyanide ligand which is coordinated to another Mn(II) center [10]. In addition, there are several compounds in which two manganese atoms are bridged by a cyanide moiety [11]. Nevertheless, it has to be pointed out that all but one [10b] of these compounds exhibit either two Mn(I) or two Mn(II) centers which makes the anion of **3** only the second structurally characterised mixed valence compound of this type. The search is completed by a number of complexes in which a manganese center and another main group or transition metal are bridged by a cyanide ligand [10,12].

In connection with the synthesis of *cis*- and *trans*- $[\text{Fe}(\text{tBuNC})_4(\text{CN})_2]$ we recognized that this reaction

Table 1
Selected bond lengths [pm] and angles [degr] of **1b**, **3–5**

1b							
Mn–C1	190.3(3)	Mn–C6	191.0(3)	Mn–C11	191.7(3)	Mn–C16	190.9(3)
Mn–C21	200.3(3)	Mn–C22	179.7(3)	C1–N1	116.1(3)	C6–N2	116.0(3)
C11–N3	116.0(3)	C16–N4	115.5(3)	C21–N5	115.4(3)	C22–O1	115.5(3)
N5–H1w1	193.6(6)	N5–H2wa ^a	218.8(7)				
C1–Mn–C6	86.9(1)	C1–Mn–C11	172.2(1)	C1–Mn–C16	92.1(1)	C1–Mn–C21	89.4(1)
C1–Mn–C22	92.0(1)	C6–Mn–C11	86.8(1)	C6–Mn–C16	176.00(1)	C6–Mn–C21	88.5(1)
C6–Mn–C22	91.8(1)	C11–Mn–C16	93.6(1)	C11–Mn–C21	85.9(1)	C11–Mn–C22	92.7(1)
C16–Mn–C21	87.7(1)	C16–Mn–C22	92.1(1)	C21–Mn–C22	178.6(1)	Mn–C1–N1	175.7(2)
Mn–C6–N2	179.6(3)	Mn–C11–N3	175.0(2)	Mn–C16–N4	179.2(2)	Mn–C21–N5	178.4(3)
Mn–C22–O1	179.5(3)						
3							
C1–C2	153.9(3)	C2–C3	148.3(3)	C3–C4	136.9(3)	C4–C5	147.7(3)
C5–C1	154.2(3)	C2–N1	127.3(3)	C3–N2	139.1(3)	C4–N3	140.6(3)
C5–N4	127.9(3)	C1–C6	152.3(3)				
C1–C2–C3	108.4(2)	C2–C3–C4	110.1(2)	C3–C4–C5	110.1(2)	C4–C5–C1	108.8(2)
C5–C1–C2	101.8(2)	C1–C2–N1	133.6(2)	C3–C2–N1	118.0(2)	C2–N1–C12	129.2(2)
C2–C3–N2	117.5(2)	C4–C3–N2	132.2(2)	C3–N2–C16	121.9(2)	C3–C4–N3	130.8(2)
C5–C4–N3	119.1(2)	C4–N3–C20	118.6(2)	C4–C5–N4	117.3(2)	C1–C5–N4	133.9(2)
C5–N4–C24	128.5(2)	C5–C1–C6	112.1(2)	C2–C1–C6	111.5(2)		
4							
Mn1–C1	180.7(4)	Mn1–C2	197.2(3)	Mn1–C3	190.8(3)	Mn1–C8	193.9(3)
Mn1–C13	191.2(3)	Mn1–C18	187.8(3)	C1–O1	115.4(4)	C2–N1	115.3(4)
C3–N2	116.1(4)	C8–N3	115.2(4)	C13–N4	116.0(3)	C18–N5	116.1(4)
Mn2–N1	209.1(3)	Mn2–Cl1	236.49(8)	Mn2–Cl2	235.29(9)	Mn2–Cl3	235.28(9)
Mn3–C23	181.5(3)	Mn3–C24	191.5(3)	Mn3–C29	190.7(3)	Mn3–C34	193.8(3)
Mn3–C39	191.1(3)	Mn3–C44	192.0(3)	C23–O2	114.4(4)	C24–N6	114.9(4)
C29–N7	115.5(4)	C34–N8	114.9(4)	C39–N9	115.5(4)	C44–N10	116.0(4)
C1–Mn1–C2	90.9(1)	C1–Mn1–C3	91.1(1)	C1–Mn1–C8	177.6(1)	C1–Mn1–C13	91.9(1)
C1–Mn1–C18	93.2(1)	C2–Mn1–C3	89.6(1)	C2–Mn1–C8	88.4(1)	C2–Mn1–C13	92.4(1)
C2–Mn1–C18	175.9(1)	C3–Mn1–C8	86.5(1)	C3–Mn1–C13	176.3(1)	C3–Mn1–C18	90.1(1)
C8–Mn1–C13	90.4(1)	C8–Mn1–C18	87.5(1)	C13–Mn1–C18	87.8(1)	Mn1–C1–O1	179.5(3)
Mn1–C2–N1	178.3(2)	Mn1–C3–N2	176.6(3)	Mn1–C8–N3	175.6(3)	Mn1–C13–N4	175.5(2)
Mn1–C18–N5	177.0(3)	C2–N1–Mn2	174.8(2)	N1–Mn2–Cl1	106.63(7)	N1–Mn2–Cl2	107.41(8)
N1–Mn2–Cl3	111.02(8)	C23–Mn3–C24	93.1(1)	C23–Mn3–C29	91.3(1)	C23–Mn3–C34	178.1(1)
C23–Mn3–C39	92.7(1)	C23–Mn3–C44	93.0(1)	C24–Mn3–C29	89.6(1)	C24–Mn3–C34	87.0(1)
C24–Mn3–C39	174.1(1)	C24–Mn3–C44	88.4(1)	C29–Mn3–C34	86.9(1)	C29–Mn3–C39	88.9(1)
C29–Mn3–C44	175.4(1)	C34–Mn3–C39	87.2(1)	C34–Mn3–C44	88.9(1)	C39–Mn3–C44	92.7(1)
Mn3–C23–O2	178.2(3)	Mn3–C24–N6	177.3(3)	Mn3–C29–N7	177.7(3)	Mn3–C34–N8	178.0(3)
Mn3–C39–N9	175.1(3)	Mn3–C44–N10	176.6(6)				
5							
Mn1–C1	179.7(5)	Mn1–C2	198.9(5)	Mn1–C5	190.1(5)	Mn1–C10	190.4(5)
Mn1–C15	191.4(5)	Mn1–C20	193.6(5)	C1–O1	115.7(6)	C2–N2	114.4(6)
C5–N5	116.0(6)	C10–N6	116.3(6)	C15–N7	116.2(6)	C20–N8	115.2(6)
Mn2–C3	197.8(5)	Mn2–C4	180.7(5)	Mn2–C25	191.2(5)	Mn2–C30	191.7(5)
Mn2–C35	189.9(5)	Mn2–C40	189.6(5)	C3–N3	115.0(6)	C4–O4	114.9(6)
C25–N9	116.4(6)	C30–N10	115.3(6)	C35–N11	115.6(6)	C40–N12	115.7(6)
Co–N2	198.6(4)	Co–N3	196.3(4)	Co–O2na	197.7(9)	Co–O2n2	198.4(5)
C1–Mn1–C2	173.1(2)	C1–Mn1–C5	90.4(2)	C1–Mn1–C10	92.3(2)	C1–Mn1–C15	92.8(2)
C1–Mn1–C20	94.5(2)	C2–Mn1–C5	83.0(2)	C2–Mn1–C10	85.9(2)	C2–Mn1–C15	89.0(2)
C2–Mn1–C20	92.2(2)	C5–Mn1–C10	89.4(2)	C5–Mn1–C15	89.7(2)	C5–Mn1–C20	175.0(2)
C10–Mn1–C15	174.8(2)	C10–Mn1–C20	91.6(2)	C15–Mn1–C20	88.8(2)	Mn1–C1–O1	177.0(4)
Mn1–C2–N2	170.5(4)	Mn1–C5–N5	176.8(4)	Mn1–C10–N6	177.5(4)	Mn1–C15–N7	179.1(4)
Mn1–C20–N8	178.7(4)	C3–Mn2–C4	179.1(2)	C3–Mn2–C25	86.5(2)	C3–Mn2–C30	85.4(2)
C3–Mn2–C35	89.2(2)	C3–Mn2–C40	91.7(2)	C4–Mn2–C25	94.4(2)	C4–Mn2–C30	94.4(2)
C4–Mn2–C35	91.1(2)	C4–Mn2–C40	87.4(2)	C25–Mn2–C30	88.0(2)	C25–Mn2–C35	88.6(2)
C25–Mn2–C40	178.0(2)	C30–Mn2–C35	173.7(2)	C30–Mn2–C40	91.2(2)	C35–Mn2–C40	92.1(2)
Mn2–C3–N3	176.7(4)	Mn2–C4–O4	177.8(4)	Mn2–C25–N9	177.4(4)	Mn2–C30–N10	174.7(4)
Mn2–C35–N11	178.4(4)	Mn2–C40–N12	176.6(4)	C2–N2–Co	158.4(4)	C3–N3–Co	169.7(4)
N2–Co–N3	118.7(2)	N2–Co–O2na	88.7(3)	N2–Co–O2n2	103.7(2)	N3–Co–O2na	107.4(3)
N3–Co–O2n2	121.8(2)	O2na–Co–O2n2	111.6(3)				

^a Symmetry code [1 – x, –y, 1 – z]

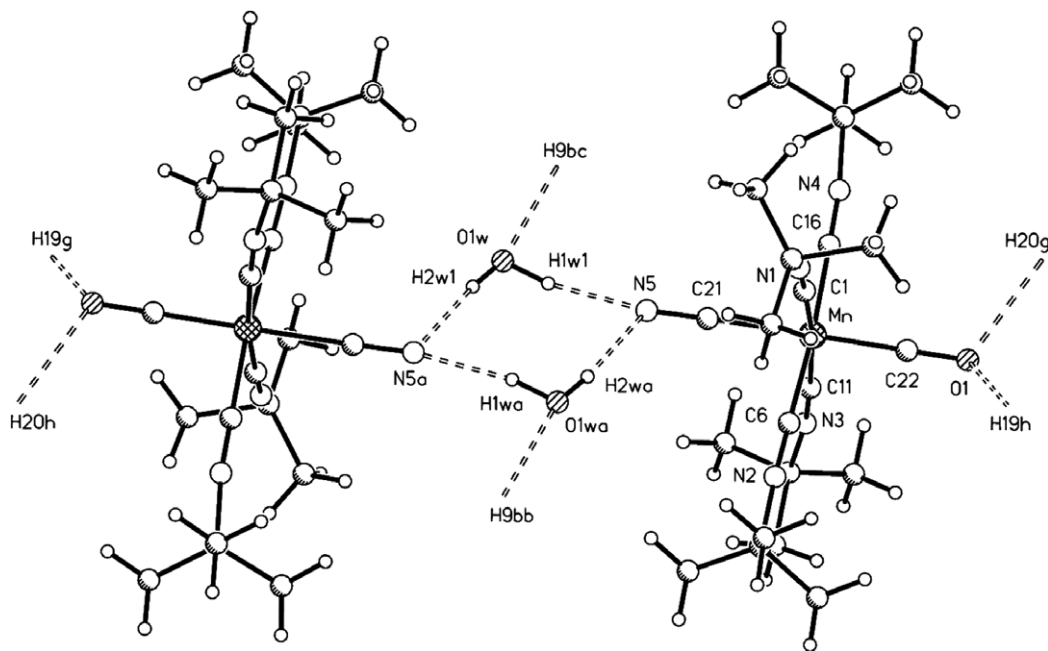


Fig. 2. Hydrogen bond network in the crystal structure of **1b**.

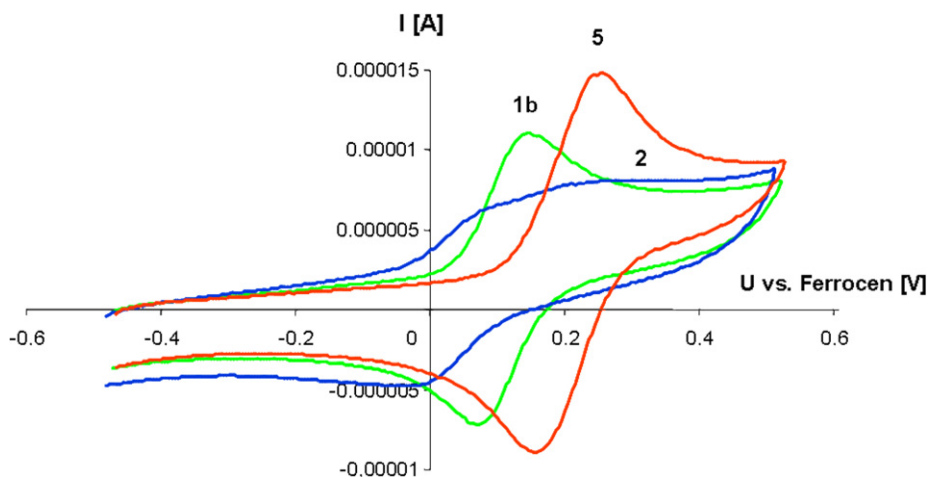


Fig. 3. Cyclic voltammetric studies of the redox behaviour of **1b**, **2** and **5** vs. ferrocene at a scan rate of 100 mV/s.

in contrast to the analogous reaction starting from ruthenium carbonyls is only successful if no carbon monoxide is present [3]. So we performed the reaction of $\text{Mn}_2(\text{CO})_{10}$ with *tert*-butyl isocyanide without any additional CO pressure. After evaporating all volatile material recrystallisation from acetone yielded a white crystalline precipitate. It turned out that this compound was not some kind of manganese coordination compound but the purely organic compound **4**. If the filtrate of this crystallization procedure is dried, the residue dissolved in THF and recrystallized from THF at low temperatures, another portion of the compounds **1a** and **1b** are obtained. The latter are therefore also formed in the reaction of $\text{Mn}_2(\text{CO})_{10}$ with *tert*-butyl isocyanide without additional CO pressure although in lower yields.

The molecular structure of **4** is presented in Fig. 6, the most important bond lengths and angles are summarized in Table 1. The carbon carbon bonds in the ring system are clearly single bonds except C3–C4 which is in the typical range of a double bond. Corresponding to this observation N1–C2 and N4–C5 also demonstrate the double bond character of the respective imino groups whereas all bonds around N2 and N3 are single bonds of amino substituents. The positions of the hydrogen atoms at N2 and N3 have been determined from the difference Fourier map. **4** therefore is a cyclopentene derivative and is obviously composed of four isocyanides and one molecule of toluene which was used as the solvent of the reaction. The four isocyanide moieties are all interconnected by new carbon carbon bonds. To the best of our knowledge

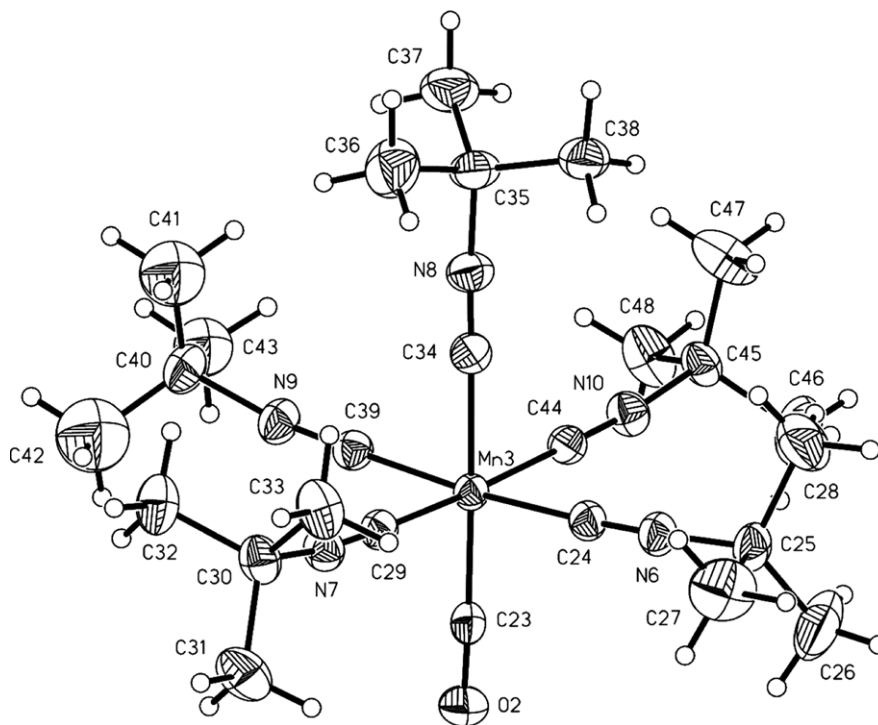


Fig. 4. Molecular structure of the cation of **3**. Displacement parameters are drawn at the 45% probability level.

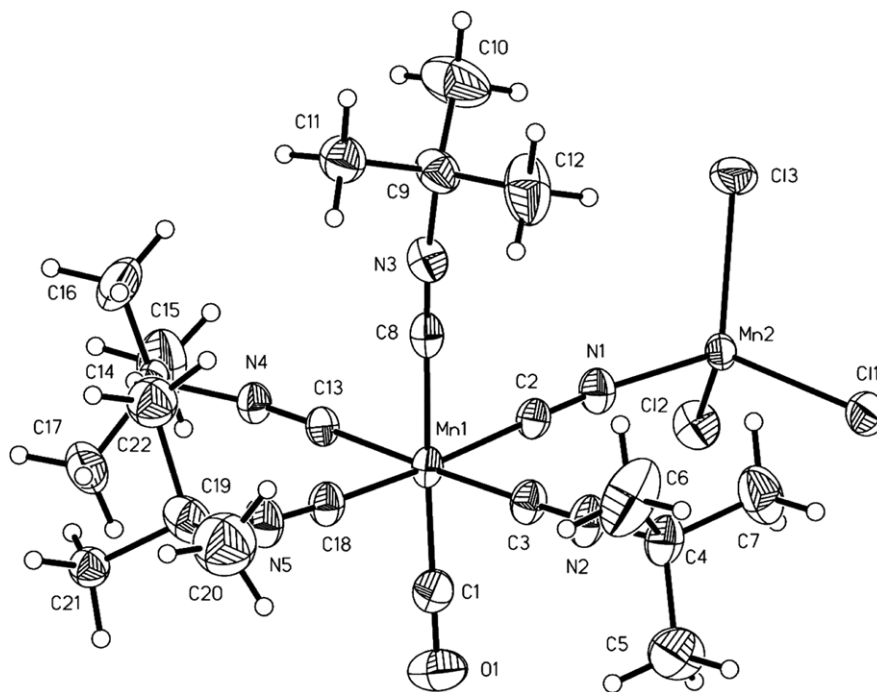


Fig. 5. Molecular structure of the anion of **3**. Displacement parameters are drawn at the 45% probability level.

this is the first 3,5-bis-imino-cyclopent-1-ene-1,2-diamine reported in the literature. The incorporation of toluene is achieved by a double benzylic C–H activation reaction. Oligomerization reactions of isocyanides leading to other types of carbocyclic or mostly heterocyclic products have already been described in the literature [13].

One of the typical reactions of transition metal cyano complexes is the formation of cyanide bridged coordination polymers [1,4]. So another proof for the identity of **1a** or **1b** as a compound with a mixed cyanide carbon monoxide coordination sphere would be the reaction with an additional transition metal fragment and the comparison

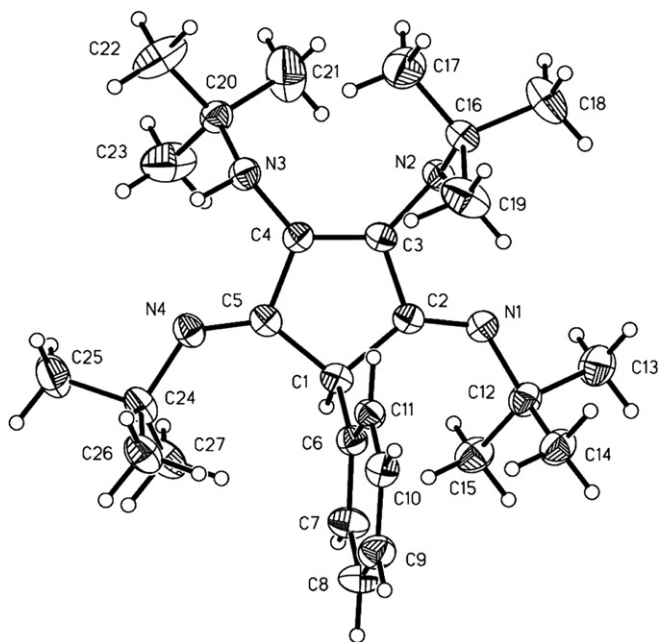


Fig. 6. Molecular structure of **4**. Displacement parameters are drawn at the 45% probability level.

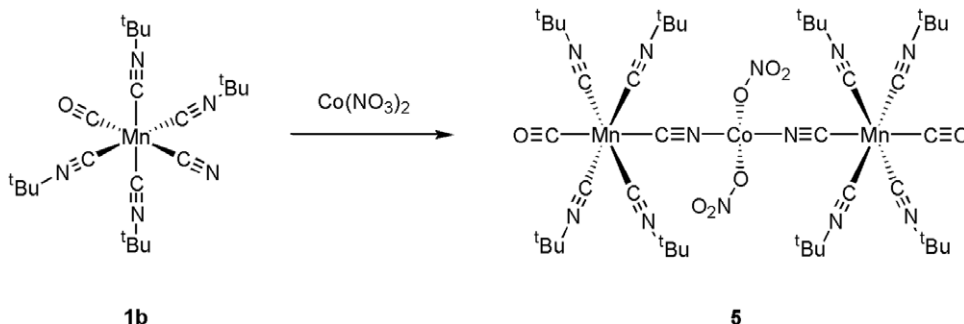
of the outcome of this reaction with the products of the same transition metal fragment with an octahedral dicyano complex. The reaction of **1b** with $\text{Co}(\text{NO}_3)_2$ results in the formation of the trinuclear compound **5** (Scheme 2). The molecular structure of **5** is presented in Fig. 7, selected bond lengths and angles are depicted in Table 1. Compound **5** is a trinuclear coordination compound in which the central cobalt atom shows a distorted tetrahedral coordination sphere and is coordinated by two nitrate anions in a η^1 -fashion as well as by the nitrogen atoms of the cyanide ligands of **1b**. Although the cyanide ligands in **5** act as bridging ligands between two transition metal centers the carbon manganese bond lengths are slightly shorter compared to the bonding situation in **1b**. In addition, the bond angles at the cyanide nitrogen atoms are not linear, most probably due to the tetrahedral ligand environment around cobalt together with steric interactions of the nitrate ions with the *tert*-butyl groups of the isocyanides. The bond lengths and angles of the CO ligands are also not affected

by the coordination of the cobalt atom the cyanide ligands in *trans*-position. In the crystal structure of **5** the carbon monoxide ligands only show intermolecular contacts towards hydrogen atoms of *tert*-butyl groups of neighboring molecules of **5** representing weak $\text{C-H}\cdots\text{O}$ interactions with $\text{H}\cdots\text{O}$ contacts above 2.7 Å.

In contrast to these observations the reaction of $\text{Co}(\text{NO}_3)_2$ with the isomeric complexes *cis*- or *trans*- $[\text{Ru}(\text{t-BuNC})_4(\text{CN})_2]$ (**6**, **8**) yields coordination polymers by the interactions of both cyanide ligands per ruthenium center with the additional cobalt atoms (Scheme 3). In both cases linear 1D-coordination polymers are produced which nevertheless differ in their supramolecular architecture due to the different stereochemistry of the starting compounds. The molecular structure of **7** which is formed in the reaction of the *trans*-isomer **6** with $\text{Co}(\text{NO}_3)_2$ is depicted in Fig. 8, the molecular structure of **9** (produced from the *cis*-isomer **8**) is presented in Fig. 9, selected bond lengths and angles are also summarized in Table 2. In analogy to the molecular structure of **5** the coordination polymers **7** and **9** show the cobalt atoms in a distorted tetrahedral coordination sphere. On the other hand, the nitrate anions in **7** and **9** are bound to the cobalt ions in a η^2 -fashion although one of the cobalt oxygen bond lengths is significantly longer than the second interaction of this type.

In the structure determination of **7** two crystallographically independent ruthenium atoms are observed each being situated on crystallographic centers of inversion. Due to the symmetry operations related to the space group $P\bar{1}$ as well as to the tetrahedral coordination geometry around the cobalt atom the supramolecular structure is a infinite zig-zag chain with a Ru-Co-Ru angle of 123.0° . In addition, one molecule of ethanol per asymmetric unit is observed in the unit cell with a site occupation factor of 0.5. The ethanol moieties each show one hydrogen bond from the OH group of the solvent molecule towards one of the oxygen atoms of a nitrate ligand as well as another hydrogen bond in which the OH group acts as the hydrogen bond acceptor from a *tert*-butyl group of one of the ruthenium complex units (Fig. 8).

Since the bond angle between the two cyanide ligands in **8** is 90° compared to 180° in **6**, it would be expected that the zig-zag chain resulting from the coordination of



Scheme 2.

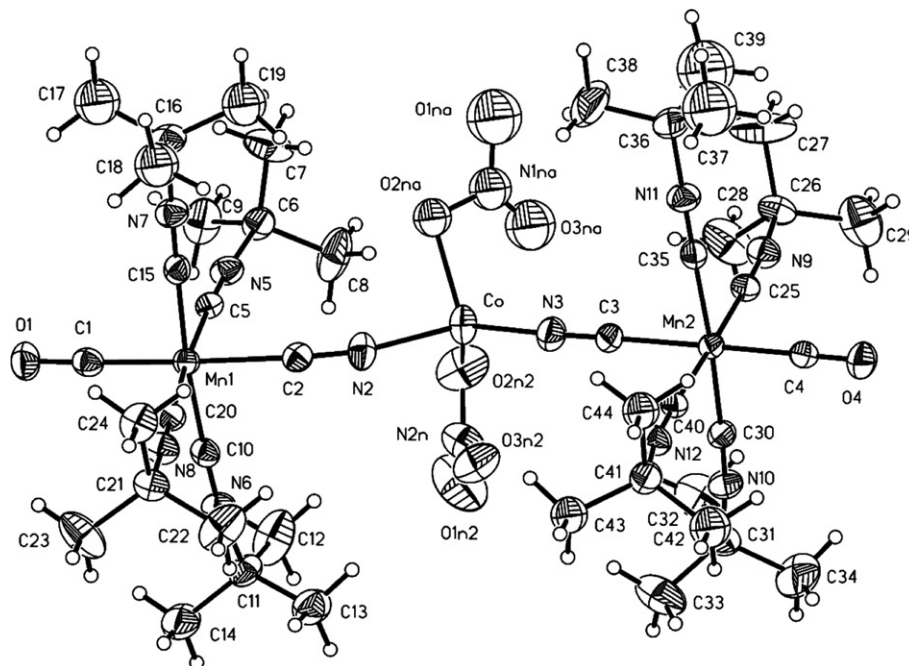
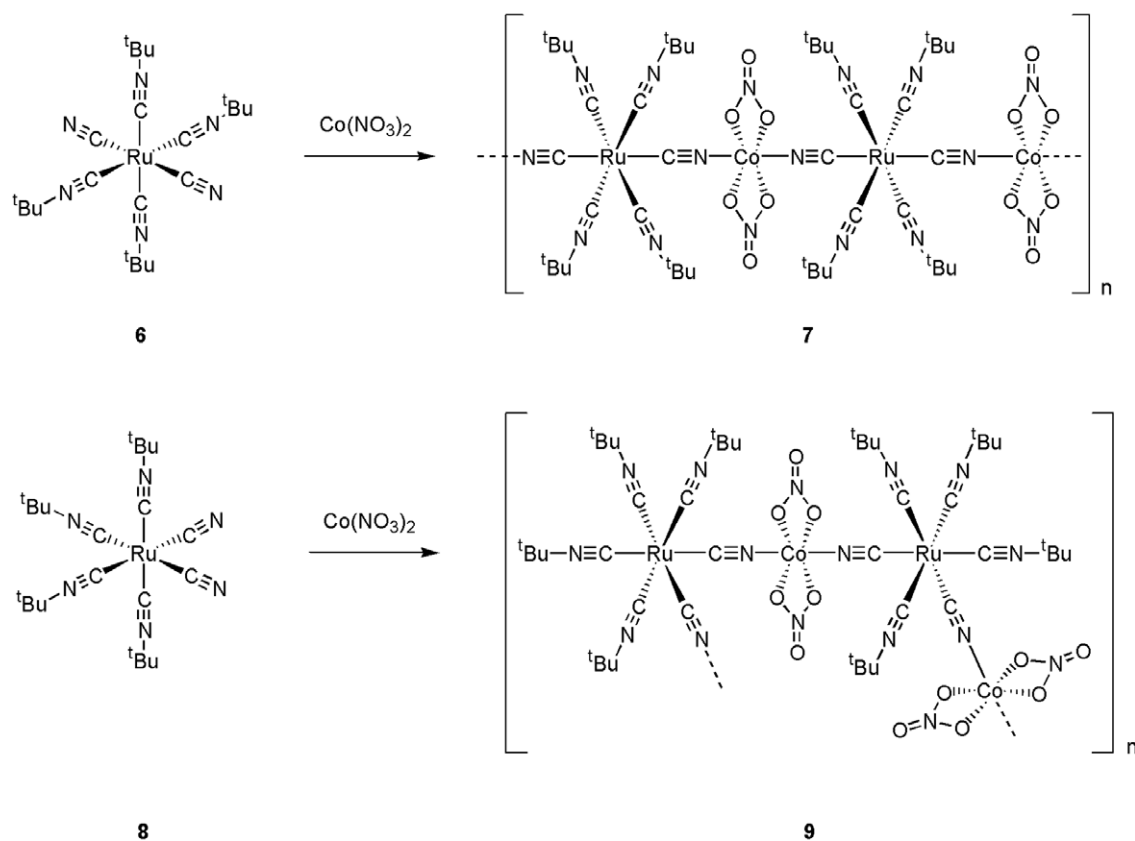


Fig. 7. Molecular structure of **5**. Displacement parameters are drawn at the 40% probability level.



Scheme 3.

$\text{Co}(\text{NO}_3)_2$ to the ruthenium complex fragments would show smaller Ru–Co–Ru angles for **9** compared to **7**. The corresponding angle measures to 113.8° and is therefore indeed smaller than the angle in **7**, although the differ-

ence is not as significant as it would have been expected. This is due to the fact that the Ru–C–N–Co axis is not linear. The other bond lengths and angles in **9** are very similar to those observed for **7** (Fig. 9 and Table 2).

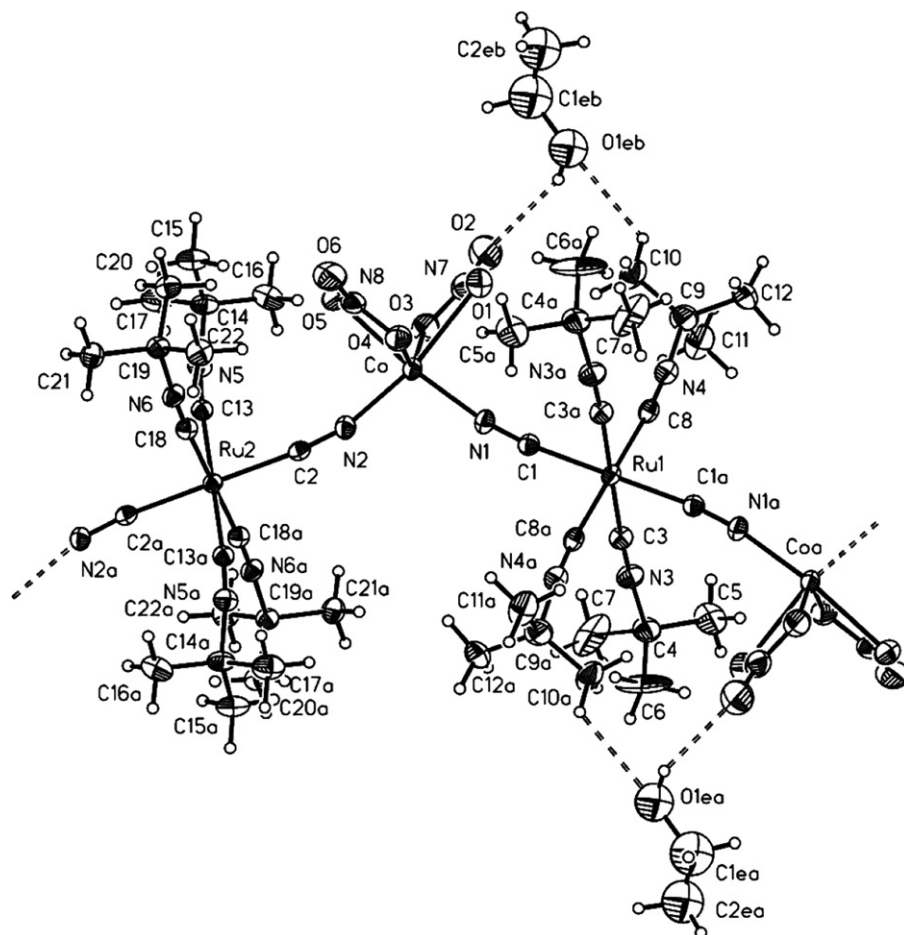


Fig. 8. Molecular structure of 7. Displacement parameters are drawn at the 35% probability level.

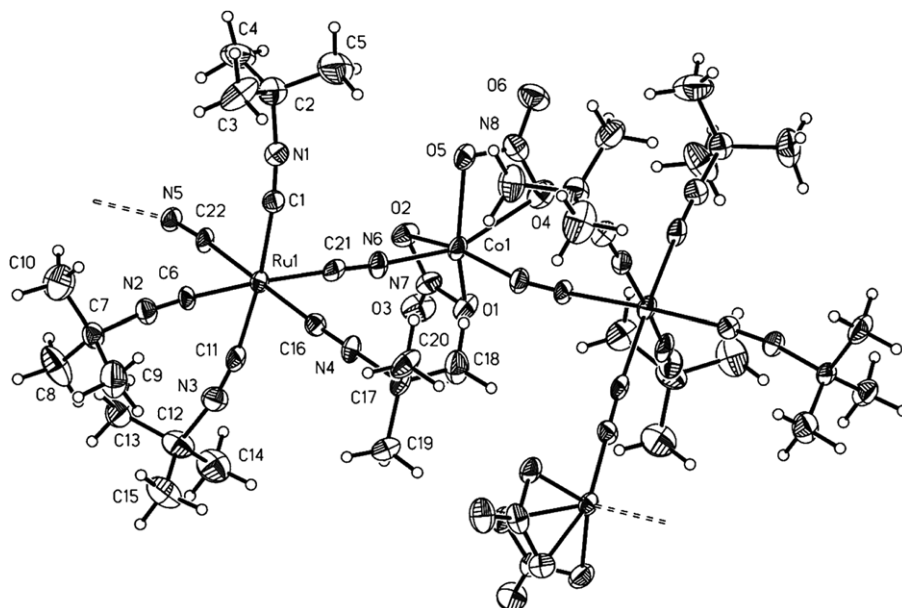


Fig. 9. Molecular structure of 9. Displacement parameters are drawn at the 35% probability level.

In summary, we have demonstrated that the reaction of manganese carbonyl with *tert*-butyl isocyanide proceeds via the reductive cleavage of isocyanide ligands together

with a concomitant oxidation of the metal centers. Nevertheless, the main products of the reaction in the presence of carbon monoxide are the Mn(I) compounds *cis*- and *trans*-

Table 2
Selected bond lengths (pm) and angles (°) of **7** and **9**

7							
Ru1–C1	204.2(6)	Ru1–C3	199.7(6)	Ru1–C8	199.2(6)	C1–N1	114.2(7)
C3–N3	114.8(7)	C8–N4	113.9(7)	Ru2–C2	204.4(6)	Ru2–C13	201.5(5)
Ru2–C18	201.5(6)	C2–N2	114.3(7)	C13–N5	113.3(7)	C18–N6	113.8(8)
Co–N1	199.4(5)	Co–N2	199.1(5)	Co–O1	240.9(5)	Co–O3	204.0(5)
Co–O4	203.0(5)	Co–O5	235.8(5)				
C1–Ru1–C3	95.0(2)	C1–Ru1–C8	86.9(2)	C3–Ru1–C8	91.9(2)	Ru1–C1–N1	172.8(5)
Ru1–C3–N3	174.0(5)	Ru1–C8–N4	175.1(5)	C2–Ru2–C13	84.8(2)	C2–Ru2–C18	87.8(2)
C13–Ru2–C18	87.1(2)	Ru2–C2–N2	173.4(5)	Ru2–C13–N5	172.8(5)	Ru2–C18–N6	176.0(5)
C1–N1–Co	167.9(5)	N1–Co–N2	103.8(2)	C2–N2–Co	165.6(5)		
9							
Ru1–C1	200(1)	Ru1–C6	201(1)	Ru1–C11	201(2)	Ru1–C16	201(1)
Ru1–C21	205(1)	Ru1–C22	204(1)	C1–N1	114(1)	C6–N2	114(1)
C11–C3	114(2)	C16–N4	114(1)	C21–N6	116(1)	C22–N5	113(1)
Co1a ^a –N5	202.0(9)	Co1–N6	199.1(9)	Co1–O1	205.1(8)	Co1–O2	236.9(7)
Co1–O4	239.0(8)	Co1–O5	203.9(8)				
C1–Ru1–C6	92.4(4)	C1–Ru1–C11	93.4(4)	C1–Ru1–C16	93.1(4)	C1–Ru1–C21	90.3(4)
C1–Ru1–C22	88.4(4)	C6–Ru1–C11	84.7(5)	C6–Ru1–C16	92.8(4)	C6–Ru1–C21	176.8(4)
C6–Ru1–C22	89.4(4)	C11–Ru1–C16	93.4(4)	C11–Ru1–C21	92.8(4)	C11–Ru1–C22	85.2(4)
C16–Ru1–C21	85.5(4)	C16–Ru1–C22	177.2(4)	C21–Ru1–C22	92.2(4)	Ru1–C1–N1	174(1)
Ru1–C6–N2	176(1)	Ru1–C11–N3	171(1)	Ru1–C16–N4	174.3(9)	Ru1–C21–N5	176.2(8)
Ru1–C22–N6	174.9(9)	C22–N5–Co1a ^a	162.1(8)	C21–N6–Co1	172.5(9)	N6–Co1–N5a ^b	104.9(3)

^a Symmetry code [$x - 0.5, y + 0.5, z - 0.5$];

^b Symmetry code [$x + 0.5, -y + 0.5, z + 0.5$]

[Mn(^tBuNC)₄(CN)(CO)] (**1a** and **1b**). If no additional CO pressure is present the formation of an organic compound produced by the oligomerisation of four *tert*-butyl isocyanide moieties together with the incorporation of one molecule of toluene, which was used as the solvent, is observed. The nature of **1a** and **1b** as compounds with a mixed carbon monoxide and cyanide ligand environment is shown by several spectroscopic techniques together with structural studies. The reaction of **1b** with Co(NO₃)₂ yields a trinuclear coordination oligomer whereas highly related complexes with another cyanide instead of the CO ligand always react via the formation of coordination polymers if they are treated with a transition metal salt. This is exemplified by the molecular structures of the compounds from the reaction of Co(NO₃)₂ with *cis*- and *trans*-[Ru(^tBuNC)₄(CN)₂].

3. Experimental

3.1. General

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. *Cis*- and *trans*-[Ru(^tBuNC)₄(CN)₂] were prepared according to the published method [2].

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 DRX 400 spectrometer (¹H: 400,13 MHz, ¹³C: 100.62 MHz, solvent as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High resolution mass spectra (HRMS) were carried out using a Finnigan MAT 95 XL spectrometer using ESI techniques. Elemental analyses were carried

out at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry of the Friedrich-Schille-University Jena. Electrochemical data were obtained by cyclic voltammetry using a PGSTAT20 potentiostat (Autolab) and an electrode stand VA 663 (Metrohm). A single-compartment three-electrode setup was composed of a platinum working electrode, a glassy carbon counter electrode and Ag/AgCl quasi-reference electrode. Measurements were performed in 0.1 M TBABF₄ acetonitrile electrolyte under nitrogen atmosphere. At the end of the measurements ferrocene was added as an internal standard and all data are reported versus ferrocene.

3.2. X-ray crystallographic studies

The structure determinations of **1b**, **3**, **4**, **5**, **7** and **9** were carried out on an Enraf Nonius Kappa CCD diffractometer, crystal detector distance 25 mm, using graphite monochromated Mo K α radiation. The crystal was mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS 86 and SHELXL 97 [14]. The molecular illustrations were drawn using the program XP [15]. The crystal and intensity data are given in Table 3.

3.3. Synthesis of *cis*- and *trans*-[Mn(^tBuNC)₄(CO)(CN)] (**1a**, **1b**), and [Mn(^tBuNC)₆]CN (**2**)

A 50 ml autoclave charged with 123 mg (0.315 mmol) dimanganesedecacarbonyl, 0.53 ml (4.725 mmol) *tert*-butylisocyanide and 5 ml toluene is pressurized with 10 bar CO

Table 3
Crystal and intensity data for the compounds **1b**, **3–5**, **7** and **9**

Compound	1	3	4	5	7	9
Formula	C ₂₂ H ₃₆ N ₅ ORu × H ₂ O	C ₄₈ H ₈₁ N ₁₀ O ₂ Cl ₃ Mn ₃	C ₂₇ H ₄₄ N ₄	C ₄₄ H ₇₂ N ₁₂ O ₈ CoMn ₂	[C ₂₂ H ₃₆ N ₈ CoRu] _n	[C ₂₂ H ₃₆ N ₈ CoRu × 0.5 C ₂ H ₅ OH] _n
Molecular weight (g mol ⁻¹)	459.51	1101.40	424.66	1065.95	668.59 ^a	691.62 ^a
Temperature (K)	183	183	183	183	183	183
Crystal colour	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal size (mm ³)	0.08 × 0.08 × 0.04	0.03 × 0.03 × 0.02	0.04 × 0.04 × 0.02	0.04 × 0.04 × 0.03	0.03 × 0.02 × 0.01	0.02 × 0.02 × 0.02
<i>a</i> (Å)	16.8870(4)	13.8640(4)	10.025(1)	11.6939(5)	10.1944(9)	9.1484(5)
<i>b</i> (Å)	9.4207(3)	20.0112(3)	10.656(1)	14.5357(7)	26.976(2)	12.1727(6)
<i>c</i> (Å)	18.9648(5)	23.8270(6)	14.060(1)	18.389(1)	12.709(1)	16.2898(9)
α (°)	90	90	102.046(5)	110.723(2)	90	94.531(2)
β (°)	113.489(2)	99.209(1)	97.795(6)	96.255(3)	105.743(4)	94.923(2)
γ (°)	90	90	110.575(6)	90.037(3)	90	103.165(3)
Volume (Å ³)	2767.1(1)	6525.2(3)	1338.9(3)	2903.6(3)	3364.0(5)	1750.8(2)
<i>Z</i>	4	4	2	2	4	2
<i>F</i> (000)	984	2324	468	1122	1372	712
ρ_{calc} (g cm ⁻³)	1.103	1.121	1.053	1.219	1.320	1.312
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Spacegroup	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
Absorption coefficient (mm ⁻¹)	0.500	0.733	0.062	0.764	0.984	0.949
θ Limit (°)	2.18 < θ < 27.47	1.60 < θ < 27.50	2.12 < θ < 27.52	2.22 < θ < 27.47	1.83 < θ < 27.40	1.73 < θ < 27.49
Reflections measured	19158	42085	7967	18895	20624	10795
Independent reflections	6326	14898	5415	12739	7557	7518
<i>R</i> _{int}	0.0324	0.0519	0.0395	0.0386	0.2140	0.0447
Observed reflections (<i>F</i> _o ² > 2 σ (<i>F</i> _o ²))	4731	9759	3412	7861	3314	5349
Number of parameters	277	622	288	613	356	433
Goodness-of-fit	1.026	1.011	1.018	1.016	1.027	1.104
<i>R</i> ₁	0.0554	0.0509	0.0689	0.0748	0.1090	0.0666
<i>wR</i> ₂	0.1569	0.1182	0.1641	0.1776	0.1910	0.1275
Largest different in peak/hole (e Å ⁻³)	1.014/−0.651	0.590/−0.503	0.270/−0.275	1.097/−0.669	1.580/−0.54	0.996/−0.840

^a Relating to one monomeric unit

and heated at 140 °C over night. After cooling all volatiles are removed in vacuo. The residue was washed with chloroform. **1a** and **1b** may be separated from the by-product [Mn(^tBuNC)₆]CN (**2**), by chromatographic work up. **1b** crystallises selectively from an acetone solution containing both isomers leaving a solution in which **1a** is enriched. Recrystallisation of **1b** from chloroform/hexane leads to crystals which were suitable for X-ray diffraction.

3.4. Spectroscopic and analytical data for **1a** and **1b**

Analysis calculated for C₂₂H₃₇N₅O_{1.5}Mn × 1/2H₂O [%]: C, 58.45; H, 8.30; N, 15.47. Found: C, 58.65; H, 8.28; N, 15.55%. m.p.: *cis*-isomer **1a**: 150 °C; *trans*-isomer **1b**: 190 °C.

MS (DEI) *m/z* (%): 441(7) ([Mn(^tBuNC)₄(CN)(CO)]H⁺); 387(6) ([Mn(^tBuNC)₄]⁺); 330(31) ([Mn(^tBuNC)₃(CN)]⁺); 274(3) ([Mn(^tBuNC)₂(CN)(CO)]H⁺); 247(66) ([Mn(^tBuNC)₂(CN)]⁺); 221(3) ([Mn(^tBuNC)₂]⁺); 191(100) ([Mn(^tBuNC)(CN)(CO)]H⁺); 164(27) ([Mn(^tBuNC)(CN)]⁺).

IR (KBr): *cis*-isomer **1a**: $\nu_{\text{as}}(\text{CH})$ 2982(s), 2937(m); $\nu_{\text{s}}(\text{CH})$ 2874(m); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2183(m), 2027(vs), 2099(vs), 2063(vs); $\nu(-\text{C}\equiv\text{O})$ 1978(vs), 1925(vs), 1883(vs); $\delta_{\text{as}}(-\text{CH}_3)$ 1458(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1398(w), 1370(s), 1233(s), 1208(s); 653(m), 640(m), 624(m) cm⁻¹; *trans*-isomer **1b**: $\nu_{\text{as}}(\text{CH})$ 2982(s), 2937(m); $\nu_{\text{s}}(\text{CH})$ 2875(m); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2101(vs), 2062(vs); $\nu(-\text{C}\equiv\text{O})$ 1903(vs), 1885(vs); $\delta_{\text{as}}(-\text{CH}_3)$ 1459(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1397(w), 1369(s), 1233(s), 1209(s); 639(m), 624(m) cm⁻¹.

^1H NMR (CD_3OD , 293 K) [ppm]: *cis*-isomer **1a**: 1.418, 1.444, 1.476 (CH_3); *trans*-isomer **1b**: 1.412 (s, CH_3).

^{13}C NMR (CDCl_3 , 293 K) [ppm]: *cis*-isomer **1a**: 30.654, 30.762, 31.07 (CH_3); 56.003, 56.869, 56.931 ($\text{C}(\text{CH}_3)_3$), carbon atoms of the cyano, isocyno and carbon monoxide ligands are not detectable; *trans*-isomer **1b**: 31.044 s (CH_3); 55.975 s ($\text{C}(\text{CH}_3)_3$); 170.206 (CN); 173.506 ($\text{C}(\text{CH}_3)_3\text{NC}$); 206.728 (CO).

3.5. Spectroscopic and analytical data for **2**

Anal. Calcd for $\text{C}_{31}\text{H}_{54}\text{N}_7\text{Mn} \times \text{CHCl}_3 \times 4 \text{CH}_3\text{OH}$ [%]: C, 52.27; H, 8.65; N, 11.85. Found: C, 52.76; H, 8.26; N, 11.41%. m.p.: 156 °C (decomp).

IR (KBr): $\nu_{\text{as}}(\text{CH})$ 2978(s), 2934(m); $\nu_{\text{s}}(\text{CH})$ 2875(m); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2092(vs), 2057(vs); $\delta_{\text{as}}(-\text{CH}_3)$ 1459(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1397(w), 1369(s), 1234(s), 1204(s); 599 (m) cm^{-1} .

^1H NMR (CDCl_3 , 293 K) [ppm]: 1.410 s (CH_3).

^{13}C NMR (CDCl_3 , 293 K) [ppm]: 31.196 s (CH_3); 56.173 s ($\text{C}(\text{CH}_3)_3$); 169.929 (CN); 174.387 ($\text{C}(\text{CH}_3)_3\text{NC}$).

3.6. Isolation of $[\text{Mn}(\text{}^t\text{BuNC})_5(\text{CO})]^+$ $[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CO})(\text{CN})\text{MnCl}_3]^-$ (**3**)

The remaining solution after the crystallization of **1b** is again dried *in vacuo* and the white precipitate is dissolved in acetone/hexane. After a few weeks crystals of **2** which are suitable for X-ray diffraction studies are obtained.

IR (KBr): $\nu_{\text{as}}(\text{CH})$ 2962(s), 2920(vs); $\nu_{\text{s}}(\text{CH})$ 2852(s); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2178(w); 2115(m), 2070(m); $\nu(-\text{C}\equiv\text{O})$ 1949(m), 1927(m); $\delta_{\text{as}}(-\text{CH}_3)$ 1460(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1400 (w), 1371(w), 1236(m), 1198(m) cm^{-1} .

MS (FAB in nba) m/z (%): 553(42) ($[\text{Mn}(\text{}^t\text{BuNC})_6]^+$); 498(100) ($[\text{Mn}(\text{}^t\text{BuNC})_5(\text{CO})]^+$); 442(15) ($[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CO})(\text{CN})\text{H}]^+$); 415(12) ($[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CO})]^+$); 387(42) ($[\text{Mn}(\text{}^t\text{BuNC})_4]^+$); 330(79) ($[\text{Mn}(\text{}^t\text{BuNC})_3(\text{CN})]^+$); 304(75) ($[\text{Mn}(\text{}^t\text{BuNC})_3]^+$); 247(99) ($[\text{Mn}(\text{}^t\text{BuNC})_2(\text{CN})]^+$); 221(53) ($[\text{Mn}(\text{}^t\text{BuNC})_2]^+$).

3.7. Synthesis of *N,N'*-di-*tert*-butyl-3,5-bis-*tert*-butylimino-4-phenyl-cyclopent-1-ene-1,2-diamine (**4**)

A 50 ml autoclave charged with 120 mg (0.308 mmol) dimanganesedecacarbonyl, 0.52 ml (4.615 mmol) *tert*-butylisocyanide and 5 ml toluene is heated without additional CO pressure at 130 °C for 24 hours. After cooling all volatiles are removed *in vacuo*. The residue is dissolved in acetone. Crystallisation at -20 °C leads to the isolation of crystalline **4**. If the filtrate of this crystallization is evaporated and the residue is dissolved in THF, another crystallisation process produces crystals of **1b**, which was shown by identical mass and IR spectra as well as the identical unit cell determined by X-ray diffraction.

Anal. Calcd for $\text{C}_{27}\text{H}_{44}\text{N}_4 \times 2 \text{MeOH} \times \text{H}_2\text{O}$ [%]: C, 68.73; H, 10.74; N, 11.06. Found: C, 69.20; H, 9.64; N, 11.24%. m.p.: 144 °C.

IR (KBr): ν (NH) 3241(m); $\nu_{\text{as}}(\text{CH})$ 3087(w), 3068(w), 3007(m); 2965(vs), 2929(m) $\nu_{\text{as}}(\text{CH})$; $\nu_{\text{s}}(\text{CH})$ 2868(w); $\nu(\text{C}=\text{N})$ 1620(vs); $\nu(\text{C}=\text{C})$ 1561(m), 1552(m); $\delta_{\text{as}}(-\text{CH}_3)$ 1452(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1390(w), 1358(m), 1221(m), 1196 (s); ν (NH) 1255(m) cm^{-1} .

MS(DEI) m/z (%) 424(40) (M); 367(55) ($\text{M}-\text{}^t\text{Bu}$); 311(47) ($\text{MH}-2\text{}^t\text{Bu}$); 255(41) ($\text{MH}_2-3\text{}^t\text{Bu}$); 199(67) ($\text{MH}_3-4\text{}^t\text{Bu}$).

High resolution MS (Micro-ESI in $\text{CHCl}_3/\text{MeOH}$): m/z (exp): 425.36387; (calcd): 425.36442.

^1H NMR(CD_2Cl_2 , 293 K) [ppm]: 1.05 s (CH_3); 1.29s (CH_3); 4.34s (C–H); 4.6b (NH); 7.19–7.34m (C_6H_5).

^{13}C NMR(CD_3OD , 293 K) [ppm]: 30.88 (CH_3); 31.11 (CH_3); 46.74 (CH); 55.73 ($-\text{C}(\text{CH}_3)_3$); 56.12 ($-\text{C}(\text{CH}_3)_3$); 127.13 (CH_{ar}); 128.83 (CH_{ar}); 129.29 (CH_{ar}); 140.41 (C_{ar}); 143.4 ($=\text{C}\cdots\text{N}$); 162.51 ($-\text{C}=\text{N}$).

3.8. Synthesis of $\{[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CO})](\mu\text{-CN})\}_2\text{Co}(\text{NO}_3)_2\}$ (**5**)

5.94 mg (0.0204 mmol) $\text{Co}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$ solved in ethanol were added to a solution of 18.0 mg (0.0408 mmol) $[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CN})(\text{CO})]$ in ethanol. The solvent was evaporated at room temperature. Crystallisation from ethanol afforded purple crystals.

Anal. Calcd for $\text{C}_{44}\text{H}_{76}\text{N}_{12}\text{O}_{10}\text{Mn}_2\text{Co} = [\text{Mn}(\text{}^t\text{BuNC})_4(\text{CO})(\text{CN})]_2\text{Co}(\text{NO}_3)_2 \times 2\text{H}_2\text{O}$ [%]: C, 47.96; H, 6.95; N, 15.25. Found: C, 47.68; H, 6.18; N, 15.19%.

IR (KBr): $\nu_{\text{as}}(\text{CH})$ 2982(m), $\nu_{\text{s}}(\text{CH})$ 2936(m); 2875(w); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2105(vs), 2063(vs); $\nu(-\text{C}\equiv\text{O})$ 1918(s); $\delta_{\text{as}}(-\text{CH}_3)$ 1459(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1369(s), 1232(m), 1209(m); $\nu(-\text{NO}_3)$ 1384(vs); 638(m), 617(m) cm^{-1} .

MS (Micro-ESI in MeOH) m/z (%): 1444(6) ($[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CN})(\text{CO})]_3 \text{Co}(\text{NO}_3)^+$); 1003(100) ($[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CN})(\text{CO})]_2 \text{Co}(\text{NO}_3)^+$); 562(37) ($[\text{Mn}(\text{}^t\text{BuNC})_4(\text{CN})(\text{CO})]\text{Co}(\text{NO}_3)^+$).

3.9. Synthesis of $\{[\text{trans-Ru}(\text{}^t\text{BuNC})_4(\text{CN})_2]\text{Co}(\text{NO}_3)_2\}_n$ (**7**)

5.9 mg (0.020 mmol) $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ solved in ethanol were added to a solution of 10.2 mg (0.020 mmol) *trans*- $[\text{Ru}(\text{}^t\text{BuNC})_4(\text{CN})_2]$ in ethanol. The solvent was evaporated at room temperature. Purple single crystals suitable for X-ray diffraction studies were obtained by crystallisation from ethanol at room temperature.

Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{N}_8\text{O}_8\text{RuCo} = [\text{Ru}(\text{}^t\text{BuNC})_4(\text{CN})\text{Co}(\text{NO}_3)_2] \times 2\text{H}_2\text{O}$ [%]: C, 37.50; H, 5.72; N, 15.90. Found: C, 37.22; H, 5.48; N, 16.14.

IR (KBr): $\nu_{\text{as}}(\text{CH})$ 2986(m), 2926(m); $\nu_{\text{s}}(\text{CH})$ 2854(m); $\nu(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2230, 2174(vs), 2137(s); $\delta_{\text{as}}(-\text{CH}_3)$ 1460(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1400(w), 1374(s), 1236(m), 1196(s); $\nu(-\text{NO}_3)$ 1384(m) cm^{-1} .

MS (Micro-ESI in Methanol) m/z (%): 1761(4) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3 \text{Co}_2(\text{NO}_3)_3^+$); 1578(87) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3 \text{Co}(\text{NO}_3)^+$); 1275(9) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2 \text{Co}_2(\text{NO}_3)_3^+$); 1093(43) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2 \text{CoNO}_3^+$);

1001(79) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_4\text{Co}^{++}$); 758(18) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3\text{Co}^{++}$); 509(100) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2\text{Na}^+$); 487(70) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]\text{H}^+$).

3.10. Synthesis of $\{[cis\text{-Ru}(\text{}^t\text{BuNC})_4(\text{CN})_2] \text{Co}(\text{NO}_3)_2\}_n$ (9)

4.6 mg (0.016 mmol) $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ solved in ethanol were added to a solution of 8.7 mg (0.016 mmol) *cis*- $[\text{Ru}(\text{}^t\text{BuNC})_4(\text{CN})_2]$ in ethanol. The solvent was evaporated at room temperature. Crystallisation in ethanol yielded purple crystals which were suitable for X-ray diffraction studies.

Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{N}_8\text{O}_8 \text{RuCo} = [\text{Ru}(\text{}^t\text{BuNC})_4(\text{CN})\text{Co}(\text{NO}_3)_2] \times 2 \text{H}_2\text{O}$ [%]: C, 37.50; H, 5.72; N, 15.90. Found: C, 37.57; H, 5.40; N, 15.99%.

IR (KBr): $\nu_{\text{as}}(\text{CH})$ 2985(m), 2924(m); $\nu_{\text{s}}(\text{CH})$ 2853(m); $\nu_{\text{C}\equiv\text{N}}(-\text{C}\equiv\text{N}/-\text{N}\equiv\text{C})$ 2230(m), 2178(vs), 2146; $\delta_{\text{as}}(-\text{CH}_3)$ 1458(m); $\delta_{\text{s}}(-\text{C}(\text{CH}_3)_3)$ 1400(w), 1373(s), 1236(m), 1197(s); $\nu(-\text{NO}_3)$ 1384(m) cm^{-1} .

MS (Micro-ESI in Methanol) *m/z* (%): 1760(16) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3\text{Co}_2(\text{NO}_3)_3^+$); 1578(36) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3 \text{Co}(\text{NO}_3)^+$); 1276(3) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2 \text{Co}_2(\text{NO}_3)_3^+$); 1093(15) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2 \text{CoNO}_3^+$); 1001(98) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_4\text{Co}^{++}$); 758(100) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_3\text{Co}^{++}$); 515(85) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]_2\text{Co}^{++}$); 509(71) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]\text{Na}^+$); 487 (46) ($[\text{Ru}(\text{CN})_2(\text{}^t\text{BuNC})_4]\text{H}^+$).

Acknowledgements

Financial support from the German Research Foundation (DFG IM 22/6-1) is gratefully acknowledged. K.H. thanks the Free State of Thuringia for a Ph.D. grant.

Appendix A. Supplementary data

CCDC 607908, 607909, 607910, 607911, 607912 and 607913 contain the supplementary crystallographic data for **9**, **1b**, **3**, **4**, **5** and **7**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.12.043](https://doi.org/10.1016/j.jorganchem.2006.12.043).

References

- [1] (a) Selected recent examples: V. Marvaud, C. Decroix, A. Sculler, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* 9 (2003) 1678; (b) V. Marvaud, C. Decroix, A. Sculler, F. Tuyras, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* 9 (2003) 1692; (c) R. Lesouëzec, J. Vaissermann, L.M. Toma, R. Carrasco, F. Lloret, M. Julve, *Inorg. Chem.* 43 (2004) 2234;
- (d) L. Toma, L.M. Toma, R. Lesouëzec, D. Armentano, G. De Munno, M. Andruh, J. Cano, F. Lloret, M. Julve, *Dalton Trans.* (2005) 1357;
- (e) C.P. Berlinguette, A. Dragulescu-Andrasi, A. Sieber, J.R. Gálan-Mascarós, H.-U. Güdel, C. Achim, K.R. Dunbar, *J. Am. Chem. Soc.* 126 (2004) 6222;
- (f) X.-Y. Chen, W. Shi, J. Xia, P. Cheng, B. Zhao, H.-B. Song, H.-G. Wang, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, *Inorg. Chem.* 44 (2005) 4263;
- (g) H.-R. Wen, C.-F. Wang, J.-L. Zuo, Y. Song, X.-R. Zeng, X.-Z. You, *Inorg. Chem.* 45 (2006) 582;
- (h) J.-N. Rebilly, L. Catala, E. Rivière, R. Guillot, W. Wernsdorfer, T. Mallah, *Chem. Comm.* (2006) 735;
- (i) C.H.M. Amijs, G.P.M. van Klink, G. van Koten, *Dalton Trans.* (2006) 308.
- [2] D. Dönnecke, W. Imhof, *Dalton Trans.* (2003) 2737.
- [3] K. Halbauer, D. Dönnecke, H. Görls, W. Imhof, *Z. Anorg. Allg. Chem.* 632 (2006) 1477.
- [4] K. Halbauer, G. Leibelng, W. Imhof, *Z. Anorg. Allg. Chem.* 632 (2006) 264.
- [5] (a) W.P. Griffith, M.J. Mockford, A.C. Skapski, *Inorg. Chim. Acta* 126 (1987) 179; (b) G.A. Carriedo, N.G. Connelly, E. Perez-Carreno, A.G. Orpen, A.L. Rieger, P.H. Rieger, V. Riera, G.M. Rosair, *J. Chem. Soc. Dalton Trans.* (1993) 3103; (c) D.B. Soria, P.J. Aymonino, *Spectrochim. Acta Part A* 55A (1999) 1243; (d) J. Jiang, A. Acunzo, S.A. Koch, *J. Am. Chem. Soc.* 123 (2001) 12109; (e) J. Jiang, S.A. Koch, *Angew. Chem.* 113 (2001) 2699; (f) S.M. Contakes, S.C.N. Hsu, T.B. Rauchfuss, S.R. Wilson, *Inorg. Chem.* 41 (2002) 1670; (g) G.M. Chiarella, D.Y. Melgarejo, S.A. Koch, *J. Am. Chem. Soc.* 128 (2006) 1416; (h) A. Kayal, T.B. Rauchfuss, *Inorg. Chem.* 42 (2003) 5046.
- [6] (a) H. Chun, E.M. Maes, R.S. Czernuszewicz, I. Bernal, *Polyhedron* 20 (2001) 2597; (b) T.A. Miller, J.C. Jeffrey, M.D. Ward, H. Adams, S.J.A. Pope, S. Faulkner, *Dalton Trans.* (2004) 1524; (c) P.V. Bernhardt, B.P. Macpherson, M. Martinez, *J. Chem. Soc. Dalton Trans.* (2002) 1435; (d) P. Guionnesau, J. Sánchez Costa, J.-F. Létard, *Acta Crystallogr. C* 60 (2004) m587.
- [7] F.H. Allen, *Acta Crystallogr. B* 58 (2002) 380.
- [8] (a) G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, 1999; (b) W. Imhof, A. Göbel, D. Braga, P. De Leonardis, E. Tedesco, *Organometallics* 18 (1999) 736; (c) D. Berger, M. Erdmann, J. Notni, W. Imhof, *CrystEngComm.* (2000) 4.
- [9] (a) D.S. Matteson, R.A. Bailey, *J. Am. Chem. Soc.* 89 (1967) 6389; (b) D.S. Matteson, R.A. Bailey, *J. Am. Chem. Soc.* 91 (1969) 1975; (c) P.M. Treichel, H.J. Mueh, *Inorg. Chem.* 16 (1977) 1167; (d) R.M. Nielsen, S. Wherland, *Inorg. Chem.* 23 (1984) 1338; (e) R.M. Nielsen, S. Wherland, *Inorg. Chem.* 24 (1985) 3458; (f) R.M. Nielsen, S. Wherland, *J. Am. Chem. Soc.* 107 (1985) 1505; (g) R.M. Nielsen, J.P. Hunt, H.W. Dodgen, S. Wherland, *Inorg. Chem.* 25 (1986) 1964; (h) M. Stebler, R.M. Nielson, W.F. Siems, J.P. Hunt, H.W. Dodgen, S. Wherland, *Inorg. Chem.* 27 (1988) 2893; (i) S.M. Godfrey, G.Q. Li, C.A. McAuliffe, P.T. Ndifon, R.G. Pritchard, *Inorg. Chim. Acta* 198-200 (1992) 23.
- [10] (a) N.G. Connelly, O.M. Hicks, G.R. Lewis, A.G. Orpen, A.J. Wood, *Chem. Commun.* (1998) 517; (b) N.G. Connelly, O.M. Hicks, G.R. Lewis, A.G. Orpen, A.J. Wood, *J. Chem. Soc. Dalton Trans.* (2000) 1637.
- [11] (a) G.A. Carriedo, M.C. Crespo, V. Riera, M.L. Valin, D. Moreiras, X. Solans, *Inorg. Chim. Acta* 121 (1986) 191;

- (b) B. Oswald, A.K. Powell, F. Rashwan, J. Heinze, H. Vahrenkamp, *Chem. Ber.* 123 (1990) 243;
- (c) K.M. Anderson, N.G. Connelly, E. Llamas-Rey, A.G. Orpen, R.L. Paul, *Chem. Commun.* (2001) 1734;
- (d) y. Tang, J. Sun, J. Chen, *Organometallics* 18 (1999) 4337.
- [12] (a) D. Bellamy, N.C. Brown, N.G. Connelly, A.G. Orpen, *J. Chem. Soc. Dalton Trans.* (1999) 3191;
- (b) N. Zhu, R. Appelt, H. Vahrenkamp, *J. Organomet. Chem.* 565 (1998) 187;
- (c) N.G. Connelly, G.R. Lewis, M.T. Moreno, A.G. Orpen, *J. Chem. Soc. Dalton Trans.* (1998) 1905;
- (d) N.G. Connelly, O.M. Hicks, G.R. Lewis, M.T. Moreno, A.G. Orpen, *J. Chem. Soc. Dalton Trans.* (1998) 1913;
- (e) V. Jacob, G. Huttner, E. Kaifer, P. Kircher, P. Rutsch, *Eur. J. Inorg. Chem.* (2001) 2783;
- (f) N.C. Brown, G.B. Carpenter, N.G. Connelly, J.G. Crossley, A. Martin, A.G. Orpen, A.L. Rieger, G.H. Worth, *J. Chem. Soc. Dalton Trans.* (1996) 3977;
- (g) K.M. Anderson, N.G. Connelly, N.J. Goodwin, G.R. Lewis, M.T. Moreno, A.G. Orpen, A.J. Wood, *J. Chem. Soc. Dalton Trans.* (2001) 1421;
- (h) F.L. Atkinson, N.C. Brown, N.G. Connelly, A.G. Orpen, A.L. Rieger, P.H. Rieger, G.M. Rosair, *J. Chem. Soc. Dalton Trans.* (1996) 1959;
- (i) A. Christofides, N.G. Connelly, H.J. Lawson, A.C. Loyns, A.G. Orpen, M.O. Simmonds, G.H. Worth, *J. Chem. Soc. Dalton Trans.* (1991) 1595;
- (j) F.L. Atkinson, A. Christofides, N.G. Connelly, H.J. Lawson, A.C. Loyns, A.G. Orpen, G.M. Rosair, G.H. Worth, *J. Chem. Soc. Dalton Trans.* (1993) 1441;
- (k) D.H. Johnson, C.L. Stern, D.F. Shriver, *Inorg. Chem.* 32 (1993) 5170;
- (l) P. Braunstein, D. Cauzzi, D. Kelly, M. Lanfranchi, A. Tirpicchio, *Inorg. Chem.* 32 (1993) 3373.
- [13] (a) T. Saegusa, N. Takahashi, Y. Ito, *J. Org. Chem.* 34 (1969) 4040;
- (b) G. Bockmair, H.P. Fritz, F.H. Löhler, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* 31B (1976) 1003;
- (c) Y. Yamamoto, H. Yamazaki, *Bull. Chem. Soc. Jpn.* 54 (1981) 787;
- (d) J.R. Clark, P.E. Fanwick, I.P. Rothwell, *J. Chem. Soc. Chem. Commun.* (1993) 1233;
- (e) T. Tanase, T. Ohizumi, K. Kobayashi, Y. Yamamoto, *Organometallics* 15 (1996) 3404;
- (f) A. Dömling, I. Ugi, *Angew. Chem.* 112 (2000) 3300;
- (g) M.A. Mironov, V.S. Mokrushin, S.S. Maltsev, *Synlett* (2003) 943;
- (h) J.C.A. Boeyens, L.M. Cook, Y. Ding, M.A. Fernandes, D.H. Reid, *Org. Biomol. Chem.* 1 (2003) 2168;
- (i) A.Y. Timoshkin, H.F. Schaefer, *J. Am. Chem. Soc.* 125 (2003) 9998;
- (j) E. Irvani, B. Neumüller, *Organometallics* 24 (2005) 842.
- [14] (a) G. Sheldrick, *SHELXS-86*, Universität Göttingen 1986;
- (b) G. Sheldrick, *SHELXL-97*, Universität Göttingen 1997.
- [15] Siemens Analytical Xray Inst. Inc., *XP - Interactive Molecular Graphics*, Vers. 4.2, 1990.