New *C*-tetrazolato complexes of rhodium(III), palladium(II) and gold(III)

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Abstract

The azido complexes $[RhCp^*(\mu-N_3)(N_3)]_2$ $(Cp^* = \eta-C_5Me_5)$, *trans*-$Rh(N_3)(CO)(PPh_3)_2$, $Na_2[Pd(N_3)_4]$, $Na_2[Pd_2(\mu-N_3)_2(N_3)_4]$ and $Na[Au(N_3)_4]$, prepared in situ from metal halide precursors and a three- to ten-fold excess of NaN_3 in water, react with aliphatic isocyanides to give a series of new metal–carbon bonded tetrazolato complexes. All azide ligands in the coordination sphere undergo this cycloaddition with isocyanides except on palladium(II) where only two tetrazol-5-ato groups are formed. In the neutral species $HAu(CN_4R)_4$ (R = ^{t}Bu (**2c**), Cy (**2d**)) presumably one of the four tetrazol-5-ato groups has been protonated to afford a tetrazol-5-ylidene (carbene) ligand. The reactivities of the isocyanides decrease in the order $CN^tBu > CNCy > CN(CH_2)_4Cl > CN$-allyl $> CNCH_2CO_2Na$; surprisingly, no reaction occurs with methylisocyanide. With *tert*-butyl isocyanide in the cold, $[Ru(\mu-N_3)(N_3)(\eta-C_{10}H_{14})]_2$ $(C_{10}H_{14}$:4-isopropyltoluene) only reacts with cleavage of the azido bridges giving rise to $[Ru(N_3)_2(\eta-C_{10}H_{14})CN^tBu]$ (**5a**), while heating of the same mixture affords a second azido-isocyanide complex, *trans*-$[Ru(N_3)_2(CN^tBu)_4]$ (**5b**), of which an X-ray structure analysis has been carried out. In some cases the reactions proceed with N_2 evolution, and rhodium complexes **6a**–**c** are also formed probably containing cyanamido ($-N\{R\}C\equiv N$) or carbodiimido ($-N=C=NR$) ligands, respectively. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Azido complexes; *C*-Tetrazolato complexes; [3 + 2]-cycloadditions; Azido–isocyanide complexes; N_2 evolution; X-ray structures

1. Introduction

The synthesis of metal–carbon bonded tetrazolates from azido complexes and isocyanides — a particularly straightforward and elegant entry to organometallic systems from inorganic ones — was first described by Beck and his group [1]. More detailed studies that also covered mechanistic considerations made clear, however, that this new reaction does not apply to any azide moiety, but is strongly dependent on the metal, the isocyanide and even the solvent [1c]. For almost 30 years no further work has been published on this type of chemistry to our knowledge. Only recently, however, the complexes $(Me_3P)_2M(Me)(CN_4R)$ (M = Pd, Pt) were obtained by Kim and coworkers from the corresponding azide and various isocyanides [2].

C-Tetrazolatorhodium(III) species, for example, were unknown to date though the isomeric *N*-tetrazolates have been prepared from azido complexes and nitriles [3]. It is interesting to note that in the same investigation the dimeric azide-bridged rhodium complex, $[RhCp^*(\mu-N_3)(N_3)]_2$ $(Cp^* = \eta-C_5Me_5)$, had also been reacted with *tert*-butyl isocyanide in acetone, though without leading to a defined product.

In the following we report on the reactions of the azido complexes **1a**–**g** (Scheme 1) with the isocyanides CNR (R = ^{t}Bu, Cy, $(CH_2)_4Cl$, allyl, CH_2CO_2Na, Me) in water. For that purpose it appeared most advantageous to prepare the azido complexes in situ from metal halide precursors and a large excess of sodium azide in aqueous solution, and to let them react directly with the isocyanide. Some reactions that proceed with evolution of dinitrogen are described.
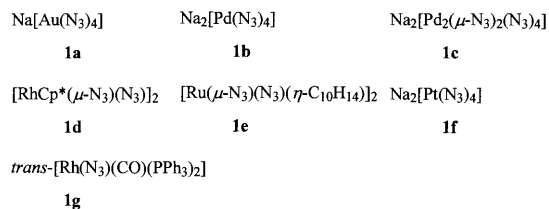
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2. Results and discussion

2.1. Alkali-tetrakis(tetrazolato)aurates and tetrakis(tetrazolato)gold acids

Tetraazidoaurate(III) (**1a**) which is prepared in situ from tetrachloroaurate(III) and a large excess of NaN_3 in dilute aqueous solution reacts with *tert*-Butyl isocyanide with gradual decolourization of the brick-red solution to give the corresponding sodium tetrakis-(tetrazol-5-ato)aurate(III) (**2a**) which separates as colourless crystals in an almost quantitative yield. In the solid state, $Na[Au(N_3)_4]$ is extremely explosive; it
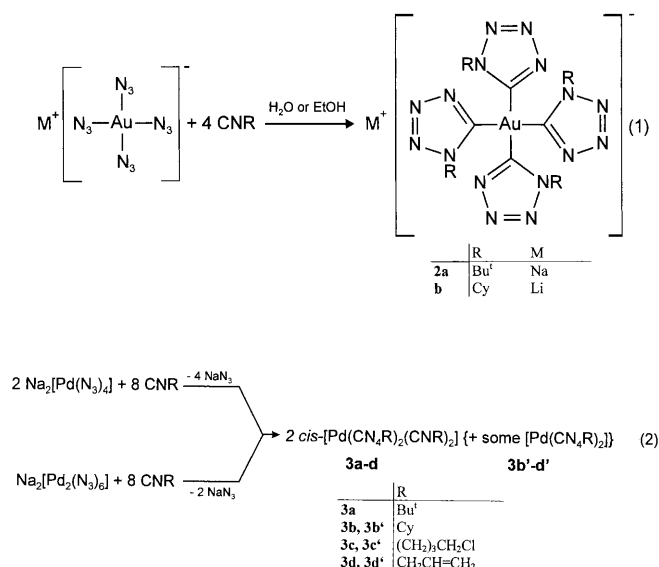
$$Na[Au(N_3)_4] \quad\quad Na_2[Pd(N_3)_4] \quad\quad Na_2[Pd_2(\mu\text{-}N_3)_2(N_3)_4]$$

$$\textbf{1a} \quad\quad\quad\quad \textbf{1b} \quad\quad\quad\quad\quad \textbf{1c}$$

$$[RhCp^*(\mu\text{-}N_3)(N_3)]_2 \quad [Ru(\mu\text{-}N_3)(N_3)(\eta\text{-}C_{10}H_{14})]_2 \quad Na_2[Pt(N_3)_4]$$

$$\textbf{1d} \quad\quad\quad\quad \textbf{1e} \quad\quad\quad\quad\quad \textbf{1f}$$

$$\textit{trans-}[Rh(N_3)(CO)(PPh_3)_2]$$

$$\textbf{1g}$$

Scheme 1. Starting materials ($\mu\text{-}N_3$ = bridging azide; Cp^* = $\eta\text{-}C_5Me_5$; $C_{10}H_{14}$ = 4-isopropyl toluene).

Table 1
Some characteristic IR data (in KBr) of the new complexes **2**–**6**

	ν(CH)	ν([M]C≡NR)	Others
2a	2976s		
2b	2935s		
2c	2979s		3600–2400s,vb; 1800–500m,vb [ν(NHN)]
2d	2938s		3600–2400s,vb; 1800–500m,vb [ν(NHN)]
3a	2977s	2216s, 2204s	
3b	2932s	2219s, 2205s	
3c	3011w, 2955s	2221s, 2210s	
3d	2925s	2197s, 2176s	1645w [ν(C=C)]
3b'	2936s		
3c'	3019w, 2960s		
3d'	2929s		1650w [ν(C=C)]
4a	2975s	2177s	
4b	2934s	2174s	
4c	3004w, 2958s	2181s	
4d	2925s	2169s	1655s [ν(C=C)]
4e	2924s	2191s	1727s,b [ν(CO$_2$Et)]
5a	2973s	2198s	2029s [ν_{as}(N$_3$)]
5b	2980s	2190s	2025s [ν_{as}(N$_3$)]
6a	2983s, 2965s		2145s, 2073s[ν_{as}(N=C=N)], [ν(N=C=N)]
6b	3050w, 2973s	2205s	2135s, 2070s[ν_{as}(N=C=N)], [ν(N=C=N)]
6c	3052w, 2965s	2201s	2126s, 2068s[ν_{as}(N=C=N)], [ν(N=C=N)]

has earlier been shown, however, that with the help of large organic cations like $AsPh_4^+$ anionic perazido complexes of almost any metal can easily be stabilized, isolated and safely handled [4]. Originally, reactions of the coordinated azide such as its cycloaddition with isocyanides have therefore been carried out with complexes of the type $AsPh_4[Au(N_3)_4]$ in organic solvents [1]. To this, the procedure described here represents a straightforward and attractive alternative leading to simple alkali salts of C-tetrazolato complexes whose spectra are free of superimposition by features of the cation.

Under identical conditions cyclohexyl isocyanide to our surprise failed to react with **1a**. Still we were able to obtain the respective lithium salt of $[Au(CN_4Cy)_4]^-$ (**2b**) by treating $Li[Au(N_3)_4]$ (again made in situ from $[AuCl_4]^-$ and LiN_3) with CNCy in ethanol. While **2a** crystallizes spontaneously from the aqueous reaction medium, **2b** can be precipitated from ethanol by adding water. Both complexes are isolated as colourless microcrystals which are practically insoluble in cold, yet readily soluble in warm water. Unlike their azide precursors, they are not explosive in the solid state despite their high content of nitrogen of about 30%. Complexes **2a** and **2b** can even be heated to 220°C (212°C), at which temperatures melting sets in with decomposition as to be seen from gas evolution. In the open flame though, they burn rapidly with little detonations. In the IR spectrum, the antisymmetric N_3 stretching vibration at 2030 cm^{-1} is clearly missing while new ν(CH) bands appear between 2900 and 3000 cm^{-1} (Table 1). All protons in **2a**, expectedly, give rise to only one signal (at δ 1.25) in the ^{1}H-NMR; the cyclohexyl groups in **2b** show the typical pattern with the *ipso*-H signal way off the rest at much lower field (Table 2).

	R	M
2a	Bu^t	Na
b	Cy	Li

$2 Na_2[Pd(N_3)_4] + 8 CNR \xrightarrow{-4 NaN_3}$

$Na_2[Pd_2(N_3)_6] + 8 CNR \xrightarrow{-2 NaN_3}$

$\rightarrow 2$ *cis-*[Pd(CN$_4$R)$_2$(CNR)$_2$] {+ some [Pd(CN$_4$R)$_2$]}   (2)

3a-d   **3b'-d'**

	R
3a	Bu^t
3b, 3b'	Cy
3c, 3c'	(CH$_2$)$_3$CH$_2$Cl
3d, 3d'	CH$_2$CH=CH$_2$

Acidification of **2a** and **2b** with dilute hydrochloric acid affords new compounds of general formula $HAu(CN_4R)_4$ (R = ^tBu (**2c**), Cy (**2d**)), which are totally insoluble in water, yet can be recrystallized from ethanol–water. Though one would expect the extra proton to be bonded to one of the tetrazole nitrogens, no $\nu(NH)$ band is observed in the usual range of 3200 ± 200 cm^{-1}; instead two extremely broad, structured IR absorption continua stretching from about 3600 to 2400 cm^{-1} and from 1800 to about 500 cm^{-1} can be made out, which is characteristic of very strong intra- or intermolecular hydrogen bridges; similar though even lower-lying IR features have recently been observed in the case of the exceedingly strong and short intermolecular hydrogen bridges present in the 'hydrogen diisocyanides', [M]C≡N–H–N≡C[M] [5].

In the ^{1}H-NMR spectra of **2c** and **2d** NH signals appear at comparatively low field which also points to hydrogen bridges. Which N atoms are involved in the N–H–N bridging, and whether these bridges are intra- or intermolecular, however, could not be settled by means of ^{15}N-NMR spectroscopy either [6]. The ^{13}C-NMR spectrum shows only one signal in the region for metal-bonded carbon atoms. Though there is no further low field-resonance that could be assigned to a carbene-carbon atom we tentatively assume that one tetrazolato ligand has been protonated at N-4 to give the neutral tris(tetrazol-5-ato)(tetrazolin-5-yliden)gold(III) complexes **2c** and **2d**. This gains support at least from the existence of two sets of *tert*-butyl carbon atoms of strikingly different intensity in the ^{13}C-NMR spectrum
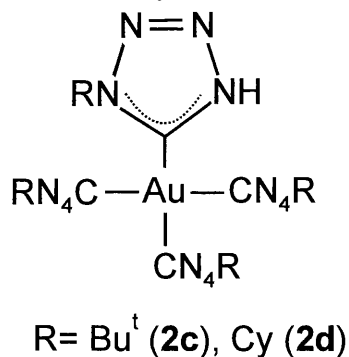

R= Bu^t (**2c**), Cy (**2d**)

Table 2
NMR data [a]

	^{1}H-NMR	^{13}C-NMR
2a [b]	1.25 (s, 36H, ^tBu)	[c]
2b [b]	1.3–2.4 (m, 40H, Cy), 4.3 (m, 4H, *ipso*-H(Cy))	[c]
2c	1.3 (s, 36H, ^tBu), 8.2 (s, 1H, NH)	156.2 (Au*C*), 59.4 (*C*Me$_3$), 32.0 (C(*C*H$_3$)$_3$)
2d	1.2–2.6 (m, 40H, Cy), 4.4 (m, 4H, *ipso*-H(Cy)), 8.25 (s, 1H, NH)	157.0 (Au*C*); 52.7, 52.6, 35.3, 28.4, 28.1 (Cy)
3a	1.2, 1.35 (2s, 18H, CN$_4$Bu^t), 1.75, 1.8 (2s, 18H, CN^{t}Bu)	162.3 (Pd*C*NBu^t(?)), 153.4, 151.3 (Pd*C*N$_4^t$Bu), 146.9 (Pd*C*N^{t}Bu(?)), 60.9–57.8 (*C*Me$_3$), 32.2–28.9 (C(*C*H$_3$)$_3$)
3b	0.9–2.6 (m, 40H, Cy), 4.3 (m, 2H, *ipso*-H(CN$_4$Cy)), 5.05 (m, 2H, *ipso*-H(CNCy))	154.0, 152.2 (Pd*C*N$_4$Cy), 55.0–28.4 (Cy)
3c	1.2–2.4 (m, 16H, CH$_2$CH$_2$CH$_2$CH$_2$), 2.8 (t, 4H, CN$_4$CH$_2$), 3.5 (t, 8H, CH$_2$Cl), 4.8 (t, 4H, CNCH$_2$)	152.2, 150.2 (Pd*C*N$_4$R), 51.0–22.8 (CH$_2$)
3d	2.7 (d, 4H, CN$_4$CH$_2$), 5.1 (t, 4H, CNCH$_2$), 5.8–6.6 (m, 12H, CH=CH$_2$)	161.2 (Pd*C*N–allyl), 155.8–154.1 (Pd*C*N$_4$–allyl), 129.3–128.4 (CH), 116.2–115.6 (CH=CH$_2$), 62.9–61.7 (NCH$_2$)
4a	0.9 (s, 15H, Cp*), 1.25 (s, 18H, CN$_4^t$Bu), 2.05 (s, 9H, CNBu^t)	156.4 (d, Rh*C*N$_4^t$Bu, ^{103}Rh-satelites, $J = 44.6$ Hz), 102.9 (*C*$_5$Me$_5$), 58.8, 58.6 (*C*Me$_3$), 30.7, 30.2 (C(*C*H$_3$)$_3$), 9.2 (C$_5$(*C*H$_3$)$_5$)
4b	0.9 (s, 15H, Cp*), 1.3–2.5 (m, 30H, Cy), 4.1 (m, 2H, *ipso*-H(CN$_4$Cy)), 5.1 (m, 1H, *ipso*-H(CNCy))	157.0 (d, Rh*C*N$_4$Cy, ^{103}Rh-satelites, $J = 42.2$ Hz), 103.0 (*C*$_5$Me$_5$), 52.4–28.7 (Cy), 9.1 (C$_5$(*C*H$_3$)$_5$)
4c	0.9 (s, 15H, Cp*), 1.2–2.6 (m, 12H, CH$_2$CH$_2$CH$_2$CH$_2$), 2.8 (t, 4H, CN$_4$CH$_2$), 3.4 (t, 6H, CH$_2$Cl), 4.9 (t, 2H, CNCH$_2$)	156.8 (d, Rh*C*N$_4$R, ^{103}Rh-satelites, $J = 44.6$ Hz), 102.5 (*C*$_5$Me$_5$), 53.6–23.3 (CH$_2$), 9.3 (C$_5$(*C*H$_3$)$_5$)
4d	0.9 (s, 15H, Cp*), 2.75 (d, 4H, CN$_4$CH$_2$), 5.1 (d, 2H, CNCH$_2$), 5.7–6.65 (m, 9H, CH=CH$_2$)	158.2 (d, RhCN$_4$–allyl, ^{103}Rh-satelites, $J = 42.2$ Hz), 103.3 (*C*$_5$Me$_5$), 132.4, 132.3 (CH), 113.2, 113.0 (CH=CH$_2$), 61.1, 60.9 (NCH$_2$)), 9.0 (C$_5$(*C*H$_3$)$_5$)
4e [b]	1.3 (s, 15H, Cp*), 3.6 (s, 4H, CN$_4$CH$_2$), 5.0 (s, 2H, CNCH$_2$)	[c]
5a	0.9 (s, 9H, Bu^t), 1.3 (d, 6H, CH(CH$_3$)$_2$), 2.3 (s, 3H, C$_6$H$_4$CH$_3$), 2.95 (m, 1H, CHMe$_2$), 7.1, 7.2 (C$_6$H$_4$)	149.2, 136.5, 128.3, 126.1 (C$_6$H$_4$+Ru*C*N^{t}Bu), 59.8 (*C*Me$_3$), 34.6 (*C*HMe$_2$), 30.5 (C(*C*H$_3$)$_3$), 24.7 (C$_6$H$_4$*C*H$_3$), 21.1 (CH(*C*H$_3$)$_2$)
5b	1.0 (s, 36H, Bu^t)	147.0 (Ru*C*N^{t}Bu), 60.2 (*C*Me$_3$), 31.6 (C(*C*H$_3$)$_3$)
6b	0.9 (s, 18H, CNBu^t), 1.3 (s, 9H, NCN^{t}Bu), 7.2 (m, 15H, Ph)	135.4 (d, Rh*C*N^{t}Bu, ^{103}Rh-satelites, $J = 36.6$ Hz), 142.5 (NCN), 138.5 (Ph, $J(^{13}$C/^{31}P) = 10.1 Hz), 134.3–128.1 (Ph), 59.8 (*C*Me$_3$), 29.4, 28.9 (C(*C*H$_3$)$_3$)
6c	1.3–2.4 (m, 30H, Cy), 4.6 (m, 2H, *ipso*-H(CNCy)), 5.2 (m, 1H, *ipso*-H(NCNCy)), 7.3 (m, 15H, Ph)	137.5 (d, Rh*C*NCy, ^{103}Rh-satelites, $J = 36.8$ Hz), 143.2 (NCN), 136.2 (Ph, $J(^{13}$C/^{31}P) = 10.2 Hz), 133.5–127.1 (Ph), 53.1–27.0 (Cy)

[a] δ values, solvent CDCl$_3$, internal standard CHCl$_3$.
[b] In DMSO.
[c] Not recorded.

of **2c** (Table 2). Complexes with mixed carbanion/carbene ligand spheres, e.g. [Co^{III}(C=NCH$_2$CH$_2$O)-{CN(H)CH$_2$CH$_2$O}$_5$](BPh$_4$)$_2$ which must have formed from tricationic hexakis(oxazolidin-2-ylidene)cobalt by loss of a proton, or [Fe^{II}Cp(CNCH$_2$CH$_2$O)(CNCH$_2$-CH$_2$OH){CN(H)CH$_2$CH$_2$O}] which assembles three different bonding states of 2-hydroxyethyl isocyanide in the same coordination sphere, are well known [7]. Like other *C*-tetrazolatogold complexes [8], compound **2c** unfortunately suffered rapid decomposition in the X-ray beam so that the data collection was given up (Section 4).

None of the other tested isocyanides gives *C*-tetrazolato complexes with [Au(N$_3$)$_4$]$^-$ under similar conditions. Methyl isocyanide and isocyano acetate caused gas evolution, however no well-defined products could be isolated; rather, metal deposition occurred after some time.

2.2. Reactions of isocyanides with homoleptic azido complexes of palladium and platinum in water

Unlike in tetraazidoaurate(III) **1a** only two azide ligands per metal atom react to give *C*-tetrazolato species in the perazidopalladium complexes **1b** and **1c**, which have also been prepared in situ from tetrachloropalladate(II) and sodium azide in water; obviously, **1b** and **1c** exist beside one another as both (AsPh$_4$)$_2$[Pd(N$_3$)$_4$] and (AsPh$_4$)$_2$[Pd$_2$(N$_3$)$_6$] are precipitated with AsPh$_4$Cl [4]. The remaining azide ligands can be replaced by isocyanide to give non-ionic compounds of the formula Pd(CN$_4$R)$_2$(CNR)$_2$ (**3a–d**) together with completely insoluble white side products, presumably coordination polymers, which analyse as [Pd(CN$_4$R)$_2$] (**3b'–d'**) and lack any high frequency IR bands. It is interesting to note that the amount of by-product increases with decreasing reactivity of the isocyanide along CN^{t}Bu > CNCy > CN(CH$_2$)$_4$Cl > CN–allyl, i.e. is highest in the case of CN–allyl. Another, yet soluble and thus probably molecular type of a binary *C*-tetrazolate, [Hg(CN$_4$R)$_2$], was obtained earlier from the reaction with loss of phosphine of Hg(N$_3$)$_2$(PPh$_3$)$_2$ with aliphatic isocyanides [1b].

Two IR bands for the CN stretching vibration prove the square planar complexes **3a–d** to exist in the *cis* configuration (Table 1). In the ^{1}H-NMR of **3a** *two* pairs of signals of slightly different intensity appear instead of the one expected for the *tert*-butyl groups on the equivalent isocyanide and tetrazole ligands. Here, possible explanations comprise hindered rotations about the Pd–C axis of the tetrazolato ligands and/or the presence of considerable amounts of the *trans* isomer. More signals than expected are also found in the ^{13}C-NMR spectra of **3a–d** where ^{13}C–^{14}N coupling is known to add to their complexity, particularly causing the [M]CNR signals to broaden and thus to be lost in the noise (Table 2) [9].

Methyl isocyanide and isocyano acetate react with the perazido palladates **1b** and **1c** much in the same way as with tetraazidoaurate, viz. with gas evolution and metal deposition. Tetraazidoplatinate(II) in aqueous solution, on the other hand, proved totally inert towards any of the isocyanides employed; after 24 h the solution had not even changed colour, and only after very long standing did platinum metal begin to deposit. These findings should be set against the successful syntheses of *C*-tetrazolates at platinum(II) *in organic media* from either azidoplatinum complexes and isocyanide, or isocyanide complexes and free azide ions [1,10].

2.3. C-Tetrazolates on the (η^5-pentamethylcyclopentadienyl)rhodium system

Contrary to the foregoing, the starting material in this paragraph, bis-μ-azido(diazido)-bis-(η-pentamethylcyclopentadienyl)dirhodium(III) (**1d**), is an isolable stable compound which precipitates on mixing aqueous solutions of [RhCp*Cl$_2$]$_2$ and NaN$_3$ [3]. To this suspension the isocyanides were added in a slight excess resulting in red, and later yellow solutions from which the products **4a–e** were extracted with dichloromethane. The graduation of isocyanide reactivities is about the same as in the reactions above with the only exception that isocyanoacetate also reacts, though to a lesser extent. Again, methylisocyanide is the exception in that it cleaves the azido bridges without advancing to the steps of insertion and cycloaddition, however. The co-existence in the same ligand sphere of potential reaction partners in compounds such as [RhCp*(N$_3$)$_2$(CNMe)] [3] or [M(N$_3$)(CO)$_5$]$^-$ (M = Cr, Mo, W) [11], on the other hand, is of substantial interest from a mechanistic point of view (cf. also [4]) [12].

	R
4a	Bu^t
b	Cy
c	(CH$_2$)$_3$CH$_2$Cl
d	CH$_2$CH=CH$_2$
e	CH$_2$CO$_2$Na
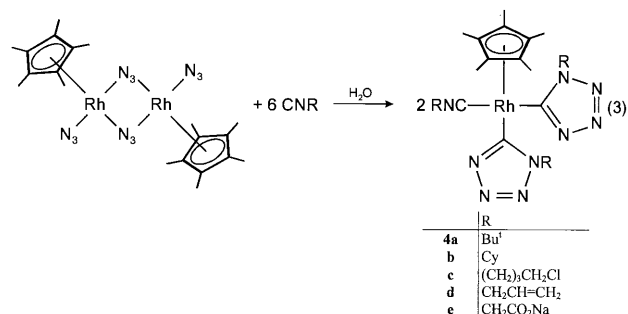
The *C*-tetrazolato complexes **4a–d** are soluble both in water and in organic media, the trisodium salt **4e** only in water, DMSO and DMF, and very moderately in methanol. Again, it should be pointed out that in organic solvents the reaction does not proceed in a clear, straightforward manner [3], and that it is not transferable a priori to other metals even if surrounded by a similar set of ligands. Thus, for example, no *C*-tetrazole formation took place in either water or dichloromethane with the

ruthenium complex **1e**, the only products being the mononuclear azido–isocyanide complexes [Ru(N$_3$)$_2$(η-C$_{10}$H$_{14}$)(CN^{t}Bu)] (**5a**) and *trans*-[Ru(N$_3$)$_2$(CN^{t}Bu)$_4$] (**5b**) (see paragraph 2.4.).

The IR spectra of **4a**–**e** typically show the strong v(CN) band of the coordinated isocyanide and the complete absence of any azide stretching vibrations. Only two ^{1}H-NMR signals appear for the two nonequivalent sets of *tert*-butyl protons in **4a** indicating that the sterically complicated situation of the square-planar palladium complex **2a** (see above) does not apply in the tetrahedral pseudooctahedral case here. The two ^{13}C lines at about δ 155 are assigned to the rhodium-bonded tetrazolato carbon atoms which experience ^{103}Rh–^{13}C coupling with reasonable J values (43 $\pm$ 1.5 Hz); in *N,O-carbene*-rhodium(III) species, for comparison, coupling constants of about 35 Hz have been determined [7]. The isocyanide–carbon signals which are expected between δ 130 and 150 have not been identified with reliability, however [13]. The mass spectra are not very revealing either; in the pos-FAB, a line can be attributed to a dinuclear species which could have formed by loss of the isocyanide ligand and bridging through the *C*-tetrazolato groups as observed in the related *N*-tetrazolato complexes [3].

An X-ray structure analysis has been undertaken of compound **4a** which only confirms the primary atomic linkage, however (Fig. 1). In the caption of Fig. 1,
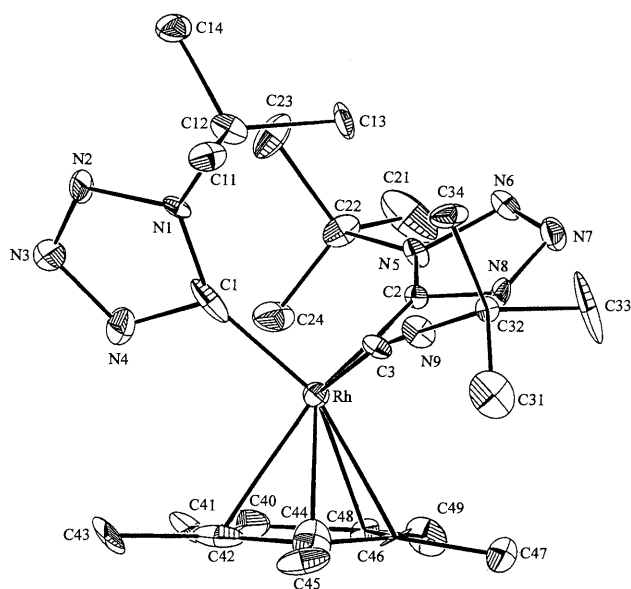

Fig. 1. ORTEP drawing of one molecule of **4a** (The bonding parameters of the independent second molecule in the asymmetric unit differ only marginally.). Selected bond distances (Å) and angles (°) (averaged values over the two molecules): Rh–Cp* 2.25; Rh–C(isocyanide) 1.92(5); Rh–C(tetrazole) 2.03(5); C–N(isocyanide) 1.18(5); C–N1 1.40(5); N1–N2 1.36(6); N2–N3 1.29(6); N3–N4 1.36(6); N4–C 1.40(6) (all tetrazole); Rh–C–N(isocyanide) 170(3); N1–C–N4 104(3); C–N1–N2 110(4); N1–N2–N3 106(4); N2–N3–N4 111(4); N3–N4–C 108(4) (all tetrazole).

average values are given for the bond lengths and angles of the four tetrazole rings in the asymmetric unit. In their tendency they seem to support a similar electronic delocalisation over the five-membered ring as has been concluded from the structure of AsPh$_4$[Au(CN$_4^i$Pr)$_4$] [8]. However, a much more precise recent X-ray structure analysis of *trans*-[PdMe(CN$_4$Cy)(PMe$_3$)$_2$] suggests a localization of π-electron density in the C1–N1 bond and a delocalization over the N2–N3–N4 part of the ring [2], remindful of the structural peculiarities of carbenoid 'activated' heterocycles [14] (Fig. 1). Due to the extensive decomposition of the crystal during the data collection the standard deviations are too high to allow any further discussion of the bonding.

2.4. Azido–isocyanide complexes

As already mentioned, the azido-bridged bis-(areneruthenium) complex **1e** prepared in situ from [Ru(μ-Cl)(Cl)(η-C$_{10}$H$_{14}$)]$_2$ (C$_{10}$H$_{14}$:4-isopropyltoluene) and sodium azide only gives the bridge-opened azido-isocyanide complex [Ru(N$_3$)$_2$(η-C$_{10}$H$_{14}$)(CN^{t}Bu)] (**5a**), though with CN^{t}Bu we have chosen the most effective isocyanide component for *C*-tetrazolate formation. Both the elemental analysis and the spectroscopic data, in particular the IR spectrum with its characteristic bands at 2029 cm^{-1} for the terminal azido ligand and at 2198 cm^{-1} for the CN group, are in accord with this notation. The most interesting ^{13}C-NMR signal, however, that of the metal-bonded isocyanide C-atom which we expected somewhere between 140 and 165 ppm, is again absent or superimposed by the lines of the aromatic system.

Even by boiling the [Ru(μ-Cl)(Cl)(η-C$_{10}$H$_{14}$)]$_2$–N$_3^-$–*tert*-butyl isocyanide mixture in water for several hours, *C*-tetrazolate formation could not be enforced; instead, arene substitution occurred to give the mononuclear azido–isocyanide complex *trans*-[Ru(N$_3$)$_2$(CN^{t}Bu)$_4$] (**5b**), which may be compared with the phosphane complexes Ru(N$_3$)$_2$(PR$_3$)$_4$ [15,16]. Complex **5b** is characterized by its IR-active (CN)- and antisymmetric (N$_3$)-stretching vibrations, and a single ^{1}H-NMR resonance for the *tert*-butyl protons. In the ^{13}C-NMR spectrum, the signal for the metal-bonded carbon atoms appears at δ 147 (Tables 1 and 2).

The results of an X-ray structure analysis of compound **5b** which had been crystallized from an ethanolic solution containing thiourea are shown in Fig. 2. Again we state the close neighbourhood within the same ligand sphere of the *cis* positioned potential reaction partners azide and isocyanide, a situation which equally prevails in the piano stool-geometries of **5a** and [RhCp*(N$_3$)$_2$(CNMe)] (cf. [3]). Ruthenium resides on a crystallographic C$_2$ axis which lies in the RuC$_4$ coordination plane bisecting a C–Ru–C angle; the two azido
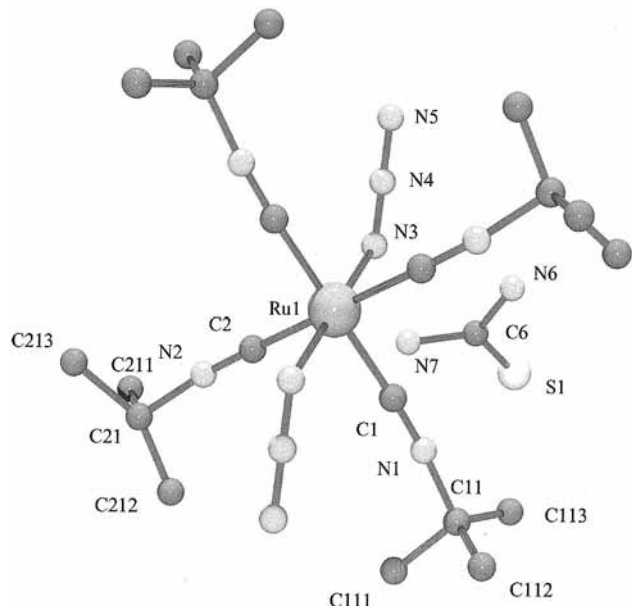
Fig. 2. ORTEP drawing of **5b** × 2 thiourea.

Table 3
Selected bond distances (Å) and angles (°) of **5b** × 2 thiourea

Ru–N3	2.14(1)	S–C6	1.73(2)
Ru–C1	1.98(1)	C6–N6	1.38(2)
Ru–C2	1.98(1)	C6–N7	1.36(3)
C1–N1	1.15(1)	Ru–N3–N4	123(1)
C2–N2	1.16(1)	Ru–C1–N1	175(1)
N1–C11	1.49(2)	Ru–C2–N2	173(1)
N2–C21	1.50(2)	C1–N1–C11	174(1)
N3–N4	1.17(1)	C2–N2–C21	166(2)
N4–N5	1.18(1)	N3–N4–N5	175(2)

ligands with their characteristically bent Ru–N–N–N atomic sequences are in *trans*-position. The Ru–N–N (average 123(1)°), Ru–C–N (average 174(1)°), C–Ru–C (average 90(2)°) and C–Ru–N (average 90(1)°) bond angles as well as the Ru–N (average 2.14(1) Å) and Ru–C(isocyanide) (average 1.98(1) Å) bond lengths are within the usual ranges (Table 3). A practically identical Ru–N distance (2.129(6) Å) has been determined for *trans*-[diazidobis{1,2-bis(diethylphosphino)ethane} ruthenium(II)] [16], while those of other azidoruthenium complexes vary between 2.093 and 2.136 Å [17–20]. Ruthenium–C(isocyanide) bonds generally appear shorter; the value found in **5b** lies within the range of 1.86–2.05 Å obtained from a literature search [21–25].

There are no unusual features in the stereochemistry of the two accompanying molecules of thiourea whose obvious function is to fill holes in the crystal lattice.

2.5. Reactions with evolution of dinitrogen

As already mentioned, dinitrogen gas is evolved in the reactions of methylisocyanide with the tetraazido

complexes of gold and palladium, but we were not able to isolate a defined product. The situation is different in the case of rhodium. Heating under reflux of **1d** with *tert*-butyl isocyanide for 5 h left a small amount of a red crystalline product with an IR spectrum in which the azide band is replaced by two strong bands at 2145 and 2073 cm^{-1}. Elemental analysis and the pos-FAB spectrum are in accord with a formulation of the compound as bis{(μ-tetrazolato-*C,N*)(cyanamido)η-pentamethylcyclopentadienylrhodium(III)} (**6a**) though we are aware that its dimeric nature might only be an artefact of mass spectrometry.

The step of *C*-tetrazolato complexes is skipped in the reactions of azido(carbonyl)bis(triphenylphosphine)-rhodium (**1g**) with *tert*-butyl or cyclohexyl isocyanide, even in the cold. In both cases, N$_2$ evolution occurs along with substitution of CO by isocyanide and partly of triphenylphosphine to give the compounds **6b** and **6c** together with a by-product analyzing as [Rh(N$_3$)-(CNR)$_2$(PPh$_3$)$_2$]. The main reaction compares well to that of azido complexes with CO to give isocyanato species [1a][12,26] and to the formation of cyanamide complexes from aminocarbyne precursors and free azide [27]. There are also interesting parallels with the recently reported conversion of *N*-isocyanamine derivatives of chromium hexacarbonyl to the corresponding cyanamides by reaction with secondary amines [28].

As in **5a**, the presence of –N=C=NR or –N(R)–C≡N ligands in the products **6b** and **6c** is suggested by the particular infrared pattern in the triple bond region (see Table 1 and above) while their composition is confirmed by elemental analyses and correct intensity ratios between the aliphatic and aromatic ^{1}H-NMR signals. The ^{13}C-NMR signal at $\delta > 140$ is tentatively assigned to the cyanamido carbon (Table 2). Unfortunately, none of the complexes presumably containing cyanamido ligands gave crystals suitable for X-ray structure analyses to date.

alternative coordination mode: [Rh]–N(R)–C≡N
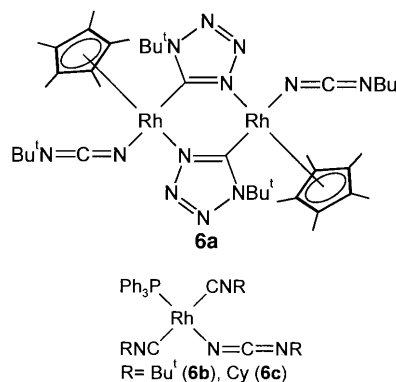
alternative coordination mode: [Rh]–N(R)–C≡N

3. Conclusions

The reactions of azido complexes with isocyanides are strongly solvent-dependent. Azidogold and palladium species react in water much in the same way as in organic solvents though some new products are obtained. They are all practically nonexplosive, i.e. much less thermally labile than the alkali perazidometallate precursors. For the formation of *C*-tetrazolates of rhodium(III), the use of water as reaction medium is essential. The reactivity of the isocyanide increases with its assumed nucleophilicity, i.e. in the order CNCH$_2$CO$_2$Na < CN–allyl < CN(CH$_2$)$_4$Cl < CNCy < CN^{t}Bu with *tert*-butyl isocyanide reacting almost quantitatively. Water-soluble methyl isocyanide is an exception in that 1-methyl-tetrazol-5-ato complexes are only obtained in organic solvents, not in water. Some reactions proceed with evolution of dinitrogen. Though several observations are in favour of the formation in rhodium complexes of cyanamido ([M]–N{R}–C≡N) or carbodiimido ligands ([M]–N=C=NR), there is no unequivocal proof for their existence[1].

4. Experimental

Most reactions were run in distilled water or air; only the reactions with the rhodium(I) complex **1g** were carried out under an atmosphere of pure argon using Schlenk-tube techniques. The organic solvents were dried, distilled and stored under argon. The starting complexes [RuCl$_2$(η-C$_{10}$H$_{14}$)]$_2$ [29] (C$_{10}$H$_{14}$: 4-isopropyltoluene), [RhCp*Cl$_2$]$_2$ [30] and *trans*-[Rh(N$_3$)(CO)(PPh$_3$)$_2$] [26b][31] were prepared by standard literature methods, the metal chlorides (RhCl$_3$·3H$_2$O, RuCl$_3$·3H$_2$O) and chlorometallates (K[AuCl$_4$], Na$_2$[PdCl$_4$], K$_2$[PtCl$_4$]) were purchased from Degussa (Hanau). IR: Perkin–Elmer model 983 and Beckman model 4240 spectrometers. NMR: Bruker AM 270. MS (EI and pos-FAB): Varian Mat 711, Varian Mat 112 S and Varian Mat CH5 DF with neutral xenon source at 3 keV. Microanalyses (C, H, N): Heraeus CHN-Rapid analyzer. Melting points (uncorrected): Gallenkamp MFB-595 apparatus.

4.1. Sodium tetrakis(1-tert-butyltetrazol-5-ato)-aurate(III) (2a)

A solution of 0.25 g (0.67 mmol) of Na[AuCl$_4$]·1/2H$_2$O in 20 ml of water was added dropwise with stirring to an aqueous solution of sodium azide (1.0 g, 15.4 mmol, 100 ml of water). *Caution: Solid sodium tetraazidoaurate is extremely explosive; any solution splashed onto the wall has to be washed with water immediately. Even concentrated aqueous solutions of Na[Au(N$_3$)$_4$] may explode!* After 30 min 0.42 ml of *tert*-butyl isocyanide were syringed into the reaction mixture, which resulted in gradual decolouration of the solution and precipitation of colourless microcrystalline Na[Au(CN$^t_4$Bu)$_4$]. The product was filtered off, washed with cold water and dried in high vacuum to give 460 mg (95%) of **2a** with m.p. 220°C (decomp.).

Anal. Found: C, 32.98; H, 4.95; N, 30.82. Calc. for C$_{20}$H$_{36}$AuN$_{16}$Na (MW 720.6): C, 33.34; H, 5.04; N, 31.10%.

4.2. Lithium tetrakis(1-cyclohexyltetrazol-5-ato)-aurate(III) (2b)

A solution of 250 mg (0.661 mmol) of K[AuCl$_4$] in 20 ml of ethanol was added dropwise with stirring to a solution of lithium azide (1.0 g) in the same solvent (100 ml). After ca. 1 h 0.54 ml (3.97 mmol) of cyclohexyl isocyanide were added which was followed by the addition of 200 ml of water after the solution had turned colourless (ca. 40 min). The solution was then concentrated in vacuo to about 100 ml and cooled to 0°C whereupon white Li[Au(CN$_4$Cy)$_4$] started to precipitate which was purified in the same way as **2a**. Yield: 350 mg (65%) of **2b** with m.p. 212°C (decomp.)

Anal. Found: C, 42.01; H, 5.62; N, 26.96. Calc. for C$_{28}$H$_{44}$AuLiN$_{16}$ (MW 808.7): C, 41.59; H, 5.48; N, 27.71%.

4.3. Tris(1-tert-Butyl-tetrazol-5-ato)(1-tert-butyl-tetrazol-5-ylidene)gold(III) (2c) and tris(1-cyclo-hexyl-tetrazol-5-ato)(1-cyclohexyl-tetrazol-5-ylidene)gold(III) (2d)

Compounds **2a** or **2b** (0.3 mmol) were dissolved in 50 ml of warm water. To this, diluted hydrochloric acid was added dropwise until no more white product precipitated. This was collected on a frit, washed with water and recrystallized from ethanol–water to give **2c** (m.p. 215°C (decomp.)) or **2d** (m.p. 221°C (decomp.), respectively, in 95% yield each.

Anal. Found for **2c**: C, 33.88; H, 5.41; N, 32.12. Calc. for C$_{20}$H$_{37}$AuN$_{16}$ (MW 698.6): C, 34.38; H, 5.34; N, 32.08%.

Anal. Found for **2d**: C, 42.21; H, 5.73; N, 27.55. Calc. C$_{28}$H$_{45}$AuN$_{16}$ (MW 802.7): C, 41.90; H, 5.65; N, 27.92%.

A colourless crystal of **2c** has been X-rayed at r.t. resulting in a substantial decay as gathered from the drop in intensity of the standard reflections and its colour change to dark-brown; the set of collected data proved inappropriate for the structure solution.

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[1] Note added in proof: Recently, carbodiimide complexes have been obtained from a palladium azide and isocyanides and crystallographically characterized: Y.-J. Kim, Y.-S. Kwak, S.-W. Lee, J. Organomet. Chem. 603 (2000) A52.

4.4. Di(tert-butyl isocyanide)bis(1-tert-butyl-tetrazol-5-ato)palladium(II) (3a)

To an aqueous solution of sodium azide (10.0 g NaN$_3$ in 100 ml of water) was added dropwise with stirring a solution of 500 mg (1.64 mmol) of Na$_2$[PdCl$_4$]·1/2H$_2$O in 30 ml of water. After 30 min 1.06 ml (10.2 mmol) of CN^{t}Bu was transferred to the reaction vessel by syringe which caused a rapid decolouration of the solution with concomitant precipitation of the product. The colourless microcrystalline precipitate was filtered, washed with water and dried in high vacuum to give 0.78 g (90%) of **3a** with m.p. 172°C (decomp.).

Anal. Found: C, 45.88; H, 6.87; N, 26.68. Calc. for C$_{20}$H$_{36}$N$_{10}$Pd (MW 523): C, 45.93; H, 6.94; N, 26.78%.

4.5. Di(cyclohexyl isocyanide)bis(1-cyclohexyl-tetrazol-5-ato)palladium(II) (3b), bis(4-chloro-Butyl isocyanide)bis[1-(4-chlorobutyl)-tetrazol-5-ato] palladium(II) (3c) and di(allyl isocyanide)bis(1-allyl-tetrazol-5-ato)palladium(II) (3d)

In their first part, the procedures are identical to the one described under Section 4.4. For further purification the white precipitates were dissolved in dichloromethane, the insoluble polymers were filtered off, and the filtrates were concentrated to about 20 ml and layered with diethyl ether. On cooling to −18°C white crystals separated.

Compound **3b** (65%; m.p. 160°C (decomp.)): Anal. Found: C, 54.02; H, 7.12; N, 21.95. Calc. for C$_{28}$H$_{44}$N$_{10}$Pd (MW 627.1): C, 53.63; H, 7.07; N, 22.33%.

Compound **3c** (45%; m.p. 165°C (decomp.)): Anal. Found: C, 35.42; H, 4.49; N, 21.12. Calc. for C$_{20}$H$_{32}$Cl$_4$N$_{10}$Pd (MW 660.8): C, 36.58; H, 4.88; N, 21.20%.

Compound **3d** (20%; m.p. 147°C (decomp.)): Anal. Found: C, 42.20; H, 4.32; N, 29.79. Calc. for C$_{16}$H$_{20}$N$_{10}$Pd (MW 458.8): C, 41.88; H, 4.39; N, 30.53%.

4.6. Bis(1-organyl-tetrazol-5-ato)palladium(II) (organyl = Cy (3b′), 4-chlorobutyl (3c′), allyl (3d′))

The insoluble coordination polymers (cf. procedure Section 4.5) were washed with dichloromethane and dried in high vacuum to give white powdery materials.

Compound **3b′** (30%; m.p. 225°C (decomp.)): Anal. Found: C, 38.95; H, 6.62; N, 25.55. Calc. for C$_{14}$H$_{22}$N$_8$Pd (MW 408.8): C, 41.13; H, 5.42; N, 27.41%.

Compound **3c′** (45%; m.p. 217°C (decomp.)): Anal. Found: C, 30.32; H, 4.01; N, 25.77. Calc. for C$_{10}$H$_{16}$Cl$_2$N$_8$Pd (MW 425.6): C, 28.22; H, 3.79; N, 26.33%.

Compound **3d′** (70%; m.p. 198°C (decomp.)): Anal. Found: C, 32.21; H, 3.51; N, 31.54. Calc. for C$_8$H$_{10}$N$_8$Pd (MW 324.6): C, 29.60, H; 3.10; N, 34.52%.

4.7. η-Pentamethylcyclopentadienyl(tert-butyl isocyanide)bis(1-tert-butyl-tetrazol-5-ato)rhodium(III) (4a)

0.53 g (0.85 mmol) of [RhCp*Cl$_2$]$_2$, dissolved in 50 ml of water, were dropped into a vigorously stirred solution of sodium azide (1.0 g) in water (100 ml) which caused the orange azido complex [RhCp*(N$_3$)$_2$]$_2$ to precipitate. After about 30 min 0.62 ml (6.0 mmol) of *tert*-butyl isocyanide was added, and the red solution was stirred for 24 h after which time it was extracted with 2 × 150 ml of dichloromethane. The extract was dried over sodium sulfate, reduced to a volume of 50 ml, and layered with ether. At −18°C yellow crystals of **4a** (m.p. 150°C (decomp.)) began to grow. Yield: 0.74 g (75%). Anal. Found: C, 52.58; H, 7.45; N, 21.94. Calc. C$_{25}$H$_{42}$N$_9$Rh (MW 571.6): C, 52.53; H, 7.41; N 22.05%.

4.8. (Cyclohexyl isocyanide)bis(1-cyclohexyl-tetrazol-5-ato)(η-pentamethylcyclopentadienyl)-rhodium(III) (4b), (4-chlorobutyl isocyanide)bis[1-(4-chlorobutyl)-tetrazol-5-ato](η-pentamethylcyclopentadienyl) rhodium(III) (4c) and (allyl isocyanide)bis(1-allyl-tetrazol-5-ato)(η-pentamethylcyclopentadienyl) rhodium(III) (4d)

In principle, **4b**–**d** were prepared as described for **4a** in Section 4.7, however, after being stirred for 24 h, the solution was warmed to ca. 50°C for 1 h before it was extracted with CH$_2$Cl$_2$. After drying with Na$_2$SO$_4$ the organic phase was evaporated to dryness in the presence of some silica gel; the impregnated material was then transferred to a chromatography column (silica gel, 30 × 3 cm) to separate the products from the unreacted and partly reacted starting complex. The products were eluted with a 1:1 mixture of dichloromethane and diethyl ether, the solutions concentrated to ca. 20 ml, layered with ether, and cooled to −18°C.

Compound **4b** (45%; m.p. 145°C (decomp.)): Anal. Found: C, 56.29; H, 7.10; N, 19.08. Calcd. C$_{31}$H$_{48}$N$_9$Rh (MW 649.7): C 57.31; H, 7.45; N, 19.40%.

Compound **4c** (40%; m.p. 142°C (decomp.)): Anal. Found: C, 43.93; H, 5.77; N, 18.55. Calc. for C$_{25}$H$_{39}$Cl$_3$N$_9$Rh (MW 674.9): C, 44.49; H 5.82; N, 18.68%.

Compound **4d** (32%; m.p. 137°C (decomp.)): Anal. Found: C, 51.10; H, 5.82; N; 24.16. Calc. for C$_{22}$H$_{30}$N$_9$Rh (MW 523.4): C, 50.48; H, 5.78; N, 24.08%.

4.9. [RhCp*(CN₄CH₂CO₂Na)₂(CNCH₂CO₂Na)] (4e)

[RhCp*Cl₂]₂ (1.0 g, 1.62 mmol), dissolved in 100 ml of water, was dropped with stirring into an aqueous solution of sodium azide (1.0 g/100 ml of H₂O) which led to a suspension of the azido complex [RhCp*(N₃)₂]₂. To this was added a solution of 1.21 g (11.3 mmol) of sodium isocyanoacetate in 20 ml of water resulting in a red solution which was stirred for 24 h, shortly heated to 50°C, and then taken to dryness in vacuo. The residue was extracted with two 100 ml portions of methanol, and the extracts were poured into a large volume of petroleum ether (40–60°C) in order to precipitate the extracted material quantitatively. The white–yellow precipitate was washed several times with ether and redissolved in methanol. This solution was concentrated to 50 ml, layered with 20 ml of ether, and cooled to −18°C for 3 days. A white material separated during this time which, however, was not the desired product. Filtration and newly layering the filtrate with ether then gave crystals of 4e (10%, m.p. 125°C (decomp.)).

Anal. Found: C, 35.99; H, 3.37; N, 18.99. Calc. for $C_{19}H_{21}N_9Na_3O_6Rh$ (MW 643.3): C, 35.47; H, 3.29; N, 19.60%.

4.10. Diazido[η-(4-isopropyl toluene)](tert-butyl isocyanide)ruthenium(II) (5a)

A solution of 0.50 g (0.82 mmol) of [RuCl₂(η-C₁₀H₁₄)]₂ in 150 ml of water was dropped into a vigorously stirred solution of sodium azide (1.0 g) in water (100 ml). After 30 min 0.58 ml (5.74 mmol) of tert-butyl isocyanide was added, and the red solution was stirred for 3 h after which time it was extracted with 2 × 150 ml of dichloromethane. The extracts were dried over sodium sulfate, reduced to a volume of 50 ml and layered with ether. At −18°C red crystals of 5a (m.p. 170°C (decomp.)) began to grow. Yield: 0.62 g (95%).

Anal. Found: C, 44.44; H, 5.52; N, 24.11. Calc. for $C_{15}H_{23}N_7Ru$ (MW 402.5): C, 44.77; H, 5.76; N, 24.36%.

4.11. Diazido[tetrakis(tert-butyl isocyanide)]ruthenium(II) (5b)

The red solution prepared from 0.50 g (0.82 mmol) of [RuCl₂(η-C₁₀H₁₄)]₂, 1.0 g of NaN₃ and 0.58 ml (5.74 mmol) of tert-butyl isocyanide in water as described under Section 4.10 was heated under reflux for 3 h during which time its colour changed to yellow. After cooling to r.t. the solution was extracted twice with 150 ml portions of dichloromethane. The organic phase was separated, dried over sodium sulfate, concentrated to a volume of 50 ml and layered with ether. At −18°C

yellow crystals of 5b (m.p. 175°C (decomp.)) started to separate. Yield: 0.55 g (75%).

Anal. Found: C, 45.91; H, 6.88; N, 26.52. Calc. $C_{20}H_{36}N_{10}Ru$ (MW 517.6): C, 46.41; H, 7.01; N, 27.06%.

4.12. Bis[μ-(1-tert-butyl-tetrazolato)-C,N]bis-[η-pentamethylcyclopentadienyl(tert-butyl-cyanamido)-rhodium(III)] (6a)

[RhCp*Cl₂]₂ (1.0 g, 1.62 mmol), NaN₃ (1.0 g in 100 ml of water) and 1.4 ml (13.5 mmol) of tert-butyl isocyanide were combined as described for 4e and then heated under reflux for 5 h, during which time the colour changed to yellow and back to red. After cooling to r.t. the solution was extracted twice with 150 ml portions of dichloromethane. The organic phase was separated, dried over sodium sulfate, concentrated to a volume of 50 ml and layered with ether. Standing at −18°C caused two compounds to crystallize which could be separated mechanically: 4a (yellow), the main product, and 6a as red crystals (5%, m.p. 115°C (decomp.)) sticking to the Schlenk tube walls.

Table 4
Crystallographic data of complexes 4a and 5b

	4a	5b
Empirical formula	$C_{25}H_{42}N_9Rh$	$C_{20}H_{36}N_{10}Ru$
		+ $2CH_4N_2S$
Formula weight (g mol⁻¹)	571.57	669.87
Crystal dimensions (mm)	$0.67 \times 0.45 \times 0.18$	0.25×0.20
		$\times 0.175$
Habit and colour	Yellow plate	Yellow, block-shaped
Crystal system	Triclinic	Monoclinic
Space group (no.)	$P\bar{1}$ (no. 1)	$P2/c$ (no. 13)
a (Å)	10.910(2)	10.268(1)
b (Å)	10.944(2)	16.248(2)
c (Å)	12.639(2)	11.821(1)
α (°)	84.114(12)	90.0
β (°)	88.891(14)	112.237(8)
γ (°)	71.774(14)	90.0
V (Å³)	1425.65	1825.47
Z	2	4
D_{calc} (g cm⁻³)	1.330	2.016
Diffractometer	Nonius CAD 4	
Radiation	Graphite-monochromatized Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	
Temperature (K)	293	
Scan type	ω–2θ	
Scan range (°)	$2 \leq 2\theta \leq 25$	$2 \leq 2\theta \leq 25$
Reflections	5231	3354
Reflections ($I > 3\sigma(I)$)	4944	3186
Parameters	619	148
Residual electron density, max (min) (e Å⁻³)	0.7 (−0.7)	1.1 (−0.7)
R (R_w)	0.048 (0.059)	0.088 (0.105)

Anal. Found: C, 50.19; H, 6.99; N 19.03. Calc. for $C_{40}H_{66}N_{12}Rh$ (MW 920.9): C, 52.17; H, 7.22; N, 18.25%.

4.13. Di(tert-butyl isocyanide)(tert-butyl-cyanamido)-(triphenylphosphine)rhodium(I) (6b) and di(cyclohexyl isocyanide)(cyclohexyl-cyanamido)(triphenylphosphine)-rhodium(I) (6c)

To 0.77 g (1.1 mmol) of $[Rh(N_3)(CO)(PPh_3)_2]$ in 20 ml of toluene was added 4.4 mmol of the respective isocyanide. After stirring for 24 h the solutions were layered with petroleum ether and cooled to $-18°C$ whereupon a yellow powder began to separate. This was extracted several times with ether, the combined extracts were concentrated to about 10 ml and kept at $-78°C$ for one week to give yellow crystals.

Compound **6b** (25%; m.p. 75°C): Anal. Found: C, 60.91; H, 6.62; N, 8.62; Calc. for $C_{33}H_{42}N_4PRh$ (MW 628.6): C, 63.05; H, 6.73; N, 8.91%.

Compound **6c** (25%; m.p. 72°C): Anal. Found: C, 64.11; H, 6.89; N, 7.78: Calc. for $C_{39}H_{48}N_4PRh$ (MW 706.7): C, 66.28; H, 6.85; N, 7.93%.

4.14. X-ray structure analyses of the complexes 4a and 5b

Suitable crystals of **4a** were obtained by layering a saturated dichloromethane solution of the complex with diethyl ether and cooling it to $-25°C$. As all attempts to grow crystals of pure **5b** of sufficient quality for the data collection had failed, crystals of composition of **5b** $\times$ 2 thiourea were grown from an ethanolic solution of **5b** which contained thiourea. Compound **4a** crystallizes in the triclinic system $P\bar{1}$ (No. 1) with two molecules in the asymmetric unit, while that of monoclinic **5b** ($P2/c$, No. 13) contains only one formula unit of **5b** $\times$ 2 thiourea. Details on crystal and intensity data are given in Table 4. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically (programs SHELXS-86[32] and XTAL-3.0 [33]). Absorption corrections (DIFABS [34]) were carried out. The extremely high standard deviations in the bonding parameters of **4a** (cf. caption of Fig. 1) are mainly caused by the rapid decomposition of the crystal in the X-ray beam which also resulted in an unfavourable data/parameter ratio in the refinement cycles. The bond lengths and angles of **5b** are given in Table 3. Final atomic positional parameters for non-hydrogen atoms, anisotropic thermal parameters, full bond distances and angles, and tables of observed and calculated structure factors are available from the authors upon request.

5. Supplementary material

Further details of the crystal structures may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), giving reference to the depository numbers CSD/408269 (**4a**), CSD/408270 (**5b**) and citing the authors and this paper.

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