Structural and Dynamic Studies on Amido-Bridged Rhodium and Iridium Complexes

Cristina Tejel, Miguel A. Ciriano,* Marta Bordonaba, José A. López, Fernando J. Lahoz, and Luis A. Oro*[a]

Abstract: Treatment of $[\{M(\mu\text{-Cl})(\text{diolefin})\}_2]$ with the lithium salts of primary and secondary amines ($LiNRR'$) in diethyl ether affords the complexes $[\{M(\mu\text{-}NRR')(\text{diolefin})\}_2]$ (M = Rh, Ir; diolefin = 1,5-cyclooctadiene (cod), tetrafluorobenzobarrelene (tfb); R′ = H, R = *t*Bu, Ph, 4-MeC_6H_4; R = R′ = Ph, 4-MeC_6H_4). Mixed-bridged chloro/amido complexes are intermediates in these syntheses, two of which, $[\{Rh(cod)\}_2(\mu\text{-}NHR)(\mu\text{-Cl})]$ (R = *t*Bu, 4-MeC_6H_4), have been isolated. Replacement of the diolefin ligands by carbon monoxide or *tert*-butyl isocyanide in selected compounds takes place with retention of the binuclear structure to give the corresponding complexes $[\{M(\mu\text{-}4\text{-}HNC_6H_4\text{-}Me)(CO)_2\}_2]$, $[\{Rh(\mu\text{-}4\text{-}HNC_6H_4Me)(CN\textit{t}Bu)_2\}_2]$ (**12**), and $[\{Rh(\mu\text{-}NPh_2)(CN\textit{t}Bu)_2\}_2]$ (**13**). Single-crystal X-ray diffraction analyses of the complexes $[\{Rh(\mu\text{-}NRR')(cod)\}_2]$ (R′ = H, R = 4-MeC_6H_4 (**3**); R = R′ = 4-MeC_6H_4 (**5**)), **12**, and **13** have shown that the conformation of the "RhN_2Rh" four-membered metallacycle is planar in **5** and folded in **3**, **12**, and **13**. The complexes with primary amides, **3** and **12**, were found to exist as the *syn*,*endo* stereoisomers. The fluxionality of the complexes with secondary amides is due to rotation of the aromatic substituents about the N–C^{ipso} bond and, in the case of **13**, to the inversion of the "RhN_2Rh" metallacycle as well. The complexes $[\{M(\mu\text{-NHR})(cod)\}_2]$ (R = Ph, 4-MeC_6H_4) were found to exist as isomeric mixtures in solution, the *syn*/*anti* ratio being 2:3 for the rhodium derivatives and 1:1 for their iridium counterparts. Again, the motion detected was due to rotation of the aromatic substituents, and could be frozen only in the case of the *syn* isomers. The complex $[\{Rh(\mu\text{-}NH\textit{t}Bu)(cod)\}_2]$ with aliphatic amido ligands was found to be the *anti* folded isomer and proved to be nonfluxional. The most common conformation of the "RhN_2Rh" metallacycle in these compounds is folded, and the preferred configuration varies from *syn* for the less encumbered compounds to *anti* on increasing the bulkiness of the bridging and ancillary ligands.

Keywords: amido ligands · fluxionality · iridium · N ligands · rhodium

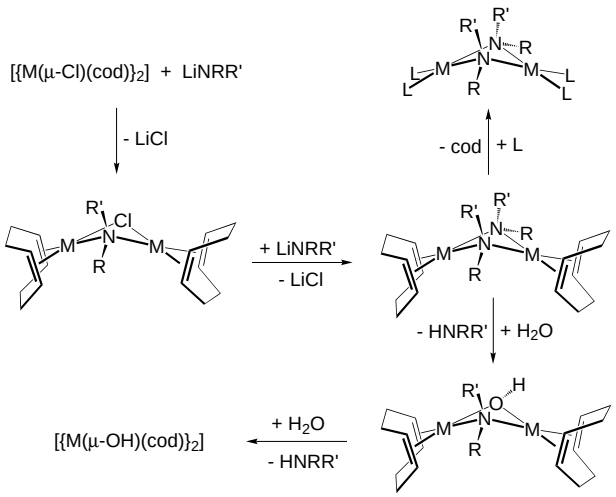
Introduction

The importance of late transition metal amido complexes is becoming increasingly recognized because they are possible intermediates in a number of interesting processes. These include stoichiometric[1] and catalytic[2] imine hydrogenations, the reduction of nitriles,[3] the palladium-catalyzed amination[4] of aryl halides and sulfonates, as well as the hydroamination[5] of activated olefins, the iridium- and rhodium-catalyzed hydroamination,[6] and the oxidative amination[7] of olefins, the latter representing a 100% atom-economic process based on readily accessible starting materials.[8] Despite this interest, only very few late transition metal amido complexes have as yet been characterized, in contrast to the renaissance of the chemistry based on early transition metal amido complexes.[9] The most studied amido compounds of rhodium and iridium are dinuclear complexes containing the chelating and bridging 1,8-diamidonaphthalene ligand[10] and mononuclear complexes with chelating bifunctional ligands,[11] while the mononuclear compounds with simple $RR'N^-$ and RNH^- ligands are very rare and reactive.[12] Dinuclear amido complexes of iridium(I)[13] and rhodium(I)[14] with simple amides ($RR'N^-$ and RNH^-) have been scarcely studied, while the related palladium and platinum chemistry is more developed[15] and has included study of the reductive elimination reactions of such complexes in the context of C–N bond-formation processes.[16] These late transition metal complexes with two simple amido bridges have been reported to exist as mixtures of several isomers in solution in some cases,[13a, 14a, 15e, 15f, 15i] while they have been described as single species in other instances.[13b, 14b, 15b] Although the existence of possible conformational equilibria in

[a] Dr. M. A. Ciriano, Prof. L. A. Oro, Dr. C. Tejel, Dr. M. Bordonaba, Dr. J. A. López, Dr. F. J. Lahoz
Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza, C.S.I.C.
50009 Zaragoza (Spain)
Fax: (+34) 976-761143
E-mail: mciriano@posta.unizar.es, oro@posta.unizar.es

  0947-6539/02/0814-3128 $ 17.50+.50/0

solution has sometimes been suggested,[14a] there is no clear picture of the configurational and conformational preferences and the fluxional motions of these compounds. It should be mentioned that some recent theoretical studies[17] have provided some guidelines on this topic. This situation prompted us to prepare some complexes of this type, and diolefin amido compounds of rhodium and iridium were envisaged as being the best suited for studying the dynamic behavior. In addition, these complexes may bear a strong resemblance to those involved in the catalytic amination of olefins. Thus, we report herein the synthesis, as well as structural and dynamic studies of dinuclear bis(μ-amido) complexes of rhodium and iridium.



Scheme 1. Synthesis and reactions of the bis(μ-amido) complexes (L = CO, CN*t*Bu).

Results

Synthesis of the complexes

Reactions of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) with two molar equivalents of the lithium salts of aliphatic and aromatic amines (LiNRR′) in diethyl ether give binuclear rhodium bis(μ-amido) complexes of the general formula $[\{Rh(\mu\text{-}NRR')(cod)\}_2]$ (R′ = H, R = *t*Bu (**1**), Ph (**2**), 4-MeC_6H_4 (**3**); R = R′ = Ph (**4**), 4-MeC_6H_4 (**5**)). The products were straightforwardly obtained, except in the case of complex **1** with the bulky aliphatic ligand *t*BuNH$^-$, for which the use of an excess of the lithium salt LiNH*t*Bu was required to force the reaction to completion. When **1** was synthesized under the conditions outlined above, the recovered solid was found to be contaminated with the mixed-ligand compound $[\{Rh(cod)\}_2(\mu\text{-}NH\textit{t}Bu)(\mu\text{-}Cl)]$ (**6**), which resulted from the fast replacement of the first chloride by one amide ligand. Actually, the metathesis of the second chloride ligand takes place slowly with the bulky *t*BuNH$^-$ group. Thus, complex **6** could be readily and independently prepared by the reaction of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and LiNH*t*Bu in a 1:1 molar ratio. In a similar manner, the complex $[\{Rh(cod)\}_2(\mu\text{-}4\text{-}HNC_6H_4Me)(\mu\text{-}Cl)]$ (**7**) was prepared by the reaction of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and LiNH(4-MeC_6H_4) in a 1:1 molar ratio (see Scheme 1). Amidorhodium complexes with diolefins other than cod, such as $[\{Rh(\mu\text{-}4\text{-}HNC_6H_4Me)(tfb)\}_2]$ (tfb = tetrafluorobenzobarrelene **8**), and the iridium derivatives $[\{Ir(\mu\text{-}NHR)(cod)\}_2]$ (R = Ph (**9**), 4-MeC_6H_4 (**10**)) were also prepared as described above.

The rhodium complexes **1**–**5** were found to react at room temperature with the water present in moist solvents to give the μ-amido/μ-hydroxo compounds $[\{Rh(cod)\}_2(\mu\text{-}NRR')(\mu\text{-}OH)]$[18] in a first step, and ultimately $[\{Rh(\mu\text{-}OH)(cod)\}_2]$, while the iridium complexes **9** and **10** were found to be more stable to hydrolysis than **1**–**5**. The hydrolysis becomes very fast on heating, but does not occur at low temperatures. This feature of the reactivity allowed the removal of LiCl from the crude products by washing with acetone/water (1:1) at low temperature (see Experimental Section).

Replacement of the diolefin ligands in two selected complexes of rhodium and iridium was found to occur with retention of the binuclear structure. Thus, complexes $[\{M(\mu\text{-}4\text{-}HNC_6H_4Me)(cod)\}_2]$ (M = Rh (**3**); Ir (**10**)) were allowed to react with carbon monoxide at atmospheric pressure to give the tetracarbonyl compounds $[\{M(\mu\text{-}4\text{-}HNC_6H_4Me)(CO)_2\}_2]$ (M = Rh, Ir) in good yields. These compounds have been previously reported as the products of reactions of *cis*-$[MCl(CO)_2(4\text{-}H_2NC_6H_4Me)]$ with sodium alkoxides.[14b]

The reactions of *tert*-butyl isocyanide with the complexes $[\{Rh(\mu\text{-}NHR)(cod)\}_2]$ (R = Ph, 4-MeC_6H_4) and $[\{Rh(\mu\text{-}NPh_2)(cod)\}_2]$ gave the compounds $[\{Rh(\mu\text{-}NHR)(CN\textit{t}Bu)_2\}_2]$ (R = Ph (**11**), 4-MeC_6H_4 (**12**)) and $[\{Rh(\mu\text{-}NPh_2)(CN\textit{t}Bu)_2\}_2]$ (**13**), which were isolated as yellow crystalline solids. Complexes **1**–**13** were characterized by analytical and spectroscopic methods, and additionally by single-crystal X-ray diffraction analysis in the case of the selected complexes **3**, **5**, **12**, and **13**.

Structural features of the bis(μ-amido) complexes: X-ray structures of $[\{Rh(\mu\text{-}4\text{-}HNC_6H_4Me)(cod)\}_2]$ (3), $[\{Rh[\mu\text{-}N(4\text{-}MeC_6H_4)_2](cod)\}_2]$ (5), $[\{Rh(\mu\text{-}4\text{-}HNC_6H_4Me)(CN\textit{t}Bu)_2\}_2]$ (12), and $[\{Rh(\mu\text{-}NPh_2)(CN\textit{t}Bu)_2\}_2]$ (13)

The complexes with primary amides, $[\{M(\mu\text{-}NHR)(L)_2\}_2]$, may exhibit two different configurations, namely *syn* and *anti*, depending on the relative disposition of the R and H groups of the bridging ligands. Additionally, the four-membered ring "RhN_2Rh" can adopt planar or folded conformations, leading to the five possibilities depicted in Figure 1. Finally, different rotamers could result from the rotation of the aromatic rings about the N–C^{ipso} bond in the complexes derived from aromatic amines.

The molecular structures of the title compounds **3**, **5**, **12**, and **13** are presented in Figure 2, Figure 3, Figure 4, and Figure 5, respectively, selected bond lengths and angles for these compounds are collected in Table 1, Table 2, Table 3, and Table 4, respectively. In each case, two rhodium centers are linked by two amido ligands, and an approximately square-planar coordination is completed by either a 1,5-cyclooctadiene group (**3** and **5**) or two *tert*-butyl isocyanide ligands (**12** and **13**). A noteworthy difference between them is the conformation of the "RhN_2Rh" four-membered metallacycle, which is nearly planar in **5** and folded in **3**, **12**, and **13**.

  0947-6539/02/0814-3129 $ 17.50+.50/0

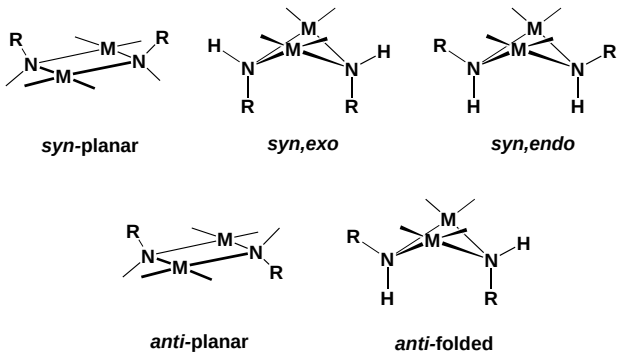


Figure 1. Possible conformations and configurations of the bis(μ-amido) complexes.

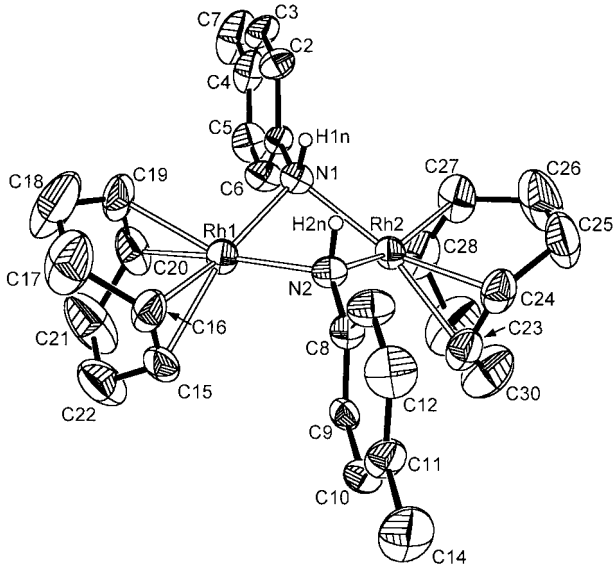


Figure 2. Molecular structure of [{Rh(μ-4-HNC$_6$H$_4$Me)(cod)}$_2$] (**3**); only hydrogen atoms bonded to the amido nitrogen atoms are shown.

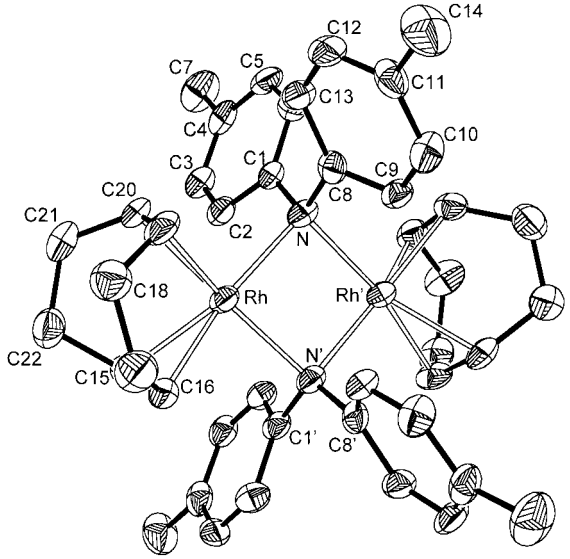


Figure 3. Molecular structure of [{Rh[μ-N(4-MeC$_6$H$_4$)$_2$](cod)}$_2$] (**5**).

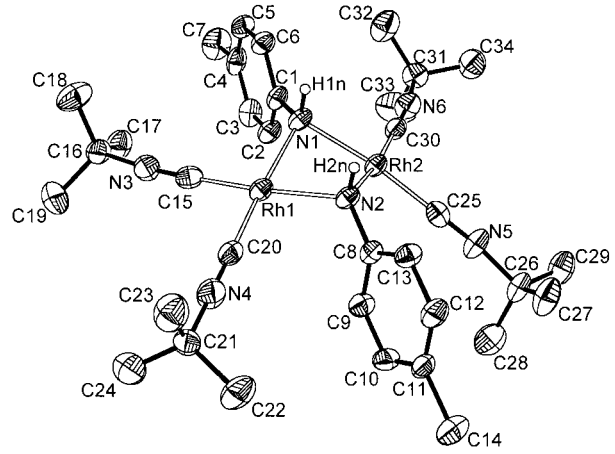


Figure 4. Molecular structure of [{Rh(μ-4-HNC$_6$H$_4$Me)(CN*t*Bu)$_2$}$_2$] (**12**); only hydrogens bonded to the amido nitrogens are shown.

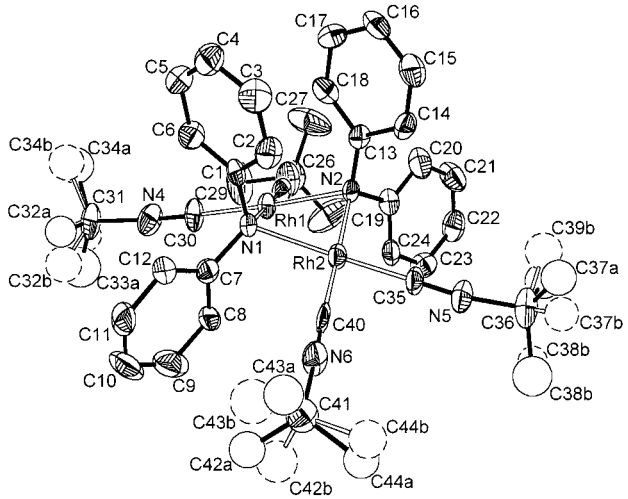


Figure 5. Molecular structure of [{Rh(μ-NPh$_2$)(CN*t*Bu)$_2$}$_2$] (**13**).

Table 1. Selected bond lengths [Å] and angles [°] for compound **3**.[a]

Rh1 ··· Rh2	3.0330(7)		
Rh1–N1	2.114(5)	Rh2–N1	2.118(5)
Rh1–N2	2.109(5)	Rh2–N2	2.105(5)
Rh1–C15	2.140(6)	Rh2–C23	2.119(7)
Rh1–C16	2.112(6)	Rh2–C24	2.106(7)
Rh1–C19	2.100(7)	Rh2–C27	2.108(6)
Rh1–C20	1.122(7)	Rh2–C28	2.131(7)
N1–C1	1.420(7)	N2–C8	1.410(7)
N1-Rh1 – N2	76.30(18)	N1-Rh2-N2	76.32(18)
N1-Rh1-M1	174.2(2)	N1-Rh2-M3	171.8(3)
N1-Rh1-M2	98.4(3)	N1-Rh2-M4	98.7(3)
N2-Rh1-M1	98.0(2)	N2-Rh2-M3	97.2(3)
N2-Rh1-M2	170.4(2)	N2-Rh2-M4	174.6(3)
M1-Rh1-M2	87.2(3)	M3-Rh2-M4	87.6(3)
Rh1-N1-Rh2	91.56(18)	Rh1-N2-Rh2	92.07(19)

[a] M1, M2, M3, and M4 represent the midpoints of the olefinic bonds C15–C16, C19–C20, C23–C24, and C27–C28, respectively.

The degree of folding, defined by the dihedral angle α between the N1-Rh1-N2 and N1-Rh2-N2 planes, was found to be similar for **3**, **12**, and **13** with α values of 131.9(2)°, 134.16(12)°, and 135.4(2)°, respectively, but α for **5** is increased to 175.0(1)°. Accordingly, complexes **3**, **12**, and **13**

  0947-6539/02/0814-3130 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 14

Table 2. Selected bond lengths [Å] and angles [°] for compound **5**[a]

Rh···Rh′	3.2965(11)		
Rh–N	2.219(5)	Rh–N′	2.211(5)
Rh–C15	2.133(7)	Rh–C19	2.150(6)
Rh–C16	2.153(6)	Rh–C20	2.136(6)
N–C1	1.446(8)	N–C8	1.437(8)
N-Rh-N′	83.71(18)	M1-Rh-M2	87.0(3)
N-Rh-M1	171.8(2)	N′-Rh-M1	94.9(2)
N-Rh-M2	95.4(2)	N′-Rh-M2	172.4(2)
Rh-N-Rh′	96.16(18)		

[a] Primed atoms are related to the unprimed ones by the symmetry operation $-x, y, 1/2-z$. M1 and M2 represent the midpoints of the olefinic bonds C15–C16 and C19–C20, respectively.

Table 3. Selected bond lengths [Å] and angles [°] for compound **12.**

Rh1···Rh2	2.9899(6)		
Rh1–N1	2.118(4)	Rh2–N1	2.107(3)
Rh1–N2	2.106(4)	Rh2–N2	2.107(4)
Rh1–C15	1.889(5)	Rh2–C25	1.886(5)
Rh1–C20	1.873(6)	Rh2–C30	1.891(6)
N1–C1	1.412(5)	N2–C8	1.413(5)
N1-Rh1-N2	79.29(14)	N1-Rh2-N2	71.51(14)
N1-Rh1-C15	94.78(18)	N1-Rh2-C25	171.92(18)
N1-Rh1-C20	172.60(17)	N1-Rh2-C30	94.16(17)
N2-Rh1-C15	173.94(18)	N2-Rh2-C25	95.82(17)
N2-Rh1-C20	94.93(17)	N2-Rh2-C30	171.46(17)
C15-Rh1-C20	91.1(2)	C25-Rh2-C30	91.0(2)
Rh1-N1-Rh2	90.08(13)	Rh1-N2-Rh2	90.42(13)

Table 4. Selected bond lengths [Å] and angles [°] for compound **13**.

Rh1···Rh2	2.9728(10)		
Rh1–N1	2.130(7)	Rh2–N1	2.181(7)
Rh1–N2	2.177(6)	Rh2–N2	2.154(7)
Rh1–C25	1.849(11)	Rh2–C35	1.872(9)
Rh1–C30	1.874(9)	Rh2–C40	1.866(11)
N1–C1	1.420(10)	N2–C13	1.419(10)
N1–C7	1.436(10)	N2–C19	1.436(10)
N1-Rh1-N2	84.3(3)	N1-Rh2-N2	83.6(3)
N1-Rh1-C25	179.5(3)	N1-Rh2-C35	177.7(4)
N1-Rh1-C30	93.1(3)	N1-Rh2-C40	95.5(3)
N2-Rh1-C25	95.3(3)	N2-Rh2-C35	94.1(3)
N2-Rh1-C30	176.0(3)	N2-Rh2-C40	178.3(3)
C25-Rh1-C30	87.3(4)	C35-Rh2-C40	86.8(4)
Rh1-N1-Rh2	87.2(3)	Rh1-N2-Rh2	86.7(2)

show similar intermetallic separations (3.0330(7) Å, 2.9899(6) Å, and 2.9728(10) Å, respectively), while the metal centers were found to be further apart in the planar complex **5** (3.2965(11) Å). The latter distance is slightly shorter than that found in the planar complex $[\{Rh(\mu\text{-}NHPh)(PPh_3)_2\}_2]$ (3.376(2) Å), the sole bis(anilido)rhodium complex reported to date.[13a]

The folded complexes derived from *p*-toluidine, $[\{Rh(\mu\text{-}4\text{-}HNC_6H_4Me)(L_2)\}_2]$ (L_2 = cod (**3**), L = CN*t*Bu (**12**)), were found to exist as the *syn*,*endo* stereoisomers in the solid state. Interestingly, the *p*-tolyl rings are almost coplanar and are located in the hypothetical plane of symmetry that would produce the equivalence of the rhodium atoms. Thus, the torsion angles C2-C1-N1-H1n (Figure 6a) and C13-C8-N2-H2n were found to be 0.6(7)° and −0.9(8)°, respectively, for complex **3**. Conventionally, and in order to simplify the following discussion, we will label this rotamer as rotamer-(0°), while we will define the rotamer-(90°) as that with the aromatic ring perpendicular to the aforementioned plane. In the isocyanide complex **12**, the *p*-tolyl rings are slightly twisted with torsion angles C6-C1-N1-H1n (Figure 6b) and C13-C8-N2-H2n of −3.3(6)° and −9.6(6)°, respectively.

Two distinct rotamers were found in the structures of the complexes derived from secondary amines $[\{Rh[\mu\text{-}N(4\text{-}MeC_6H_4)_2](cod)\}_2]$ (**5**) and $[\{Rh(\mu\text{-}NPh_2)(CN\mathit{t}Bu)_2\}_2]$ (**13**), which contain four aromatic rings. In complex **13**, the torsion angles for the equatorial rings, C12-C7-N1-C1 and C20-C19-N2-C13, were found to be 11.4(12)° and 14.3(11)°, respectively, while those for the axial rings C6-C1-N1-C7 (Figure 7a) and C14-C13-N2-C19 were found to be 76.8(10)° and 75.5(10)°, respectively.

It should be noted that the disposition of the equatorial phenyl rings in **13** and of the *p*-tolyl groups in the *syn*,*endo* **3** and **12** is approximately that defined for rotamer-(0°), which is generally observed for the related *syn*,*endo*[13b, 15g] and *anti*[14a15a–c, 15f] isomers of dinuclear complexes with bridging primary aromatic amides of rhodium, iridium, palladium, and platinum. On the contrary, the planes of the pair of axial aromatic rings in **13** show nearly the disposition defined for rotamer-(90°). For comparison purposes, the two previously established structures of anilido late transition metal complexes with a *syn*,*exo* stereochemistry show rotamers quite different to rotamer-(90°) due to intramolecular π-stacking interactions between the anilido ring and the phenyl groups of the phosphine ligands.[13a]

Finally, the complex $[\{Rh[\mu\text{-}N(4\text{-}MeC_6H_4)_2](cod)\}_2]$ (**5**), having an imposed C_2 crystallographic axis, shows torsion angles C6-C1-N-C8 (Figure 7b) and C13-C8-N-C1 of −30.1(8)° and −35.4(9)° for the two nonequivalent *p*-tolyl groups bonded to the nitrogen. This rotamer most probably represents the stereochemistry that minimizes the interligand (*p*-tolyl and cod) and intraligand (between two *p*-tolyl groups) steric repulsions in **5**.

Dynamic behavior in solution: The detection of conformational, rotational, and configurational equilibria

The species present in solution and the fluxional motions of the diolefin bis(μ-amido) complexes were identified by means of variable-temperature ^{1}H NMR spectroscopy in conjunction

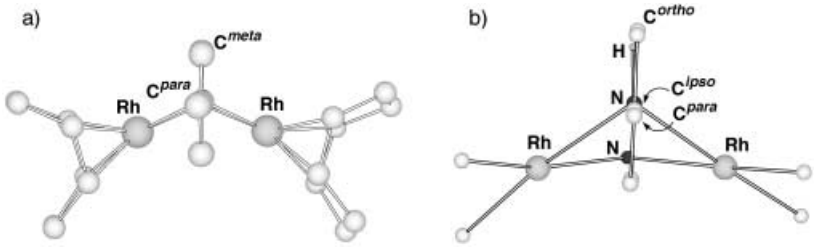


Figure 6. Newman projections along the N–C^{ipso} bond, showing the disposition of the aromatic rings in a) complex **3** (rotamer-(0°)); b) complex **12**. Only one aromatic ring is drawn.

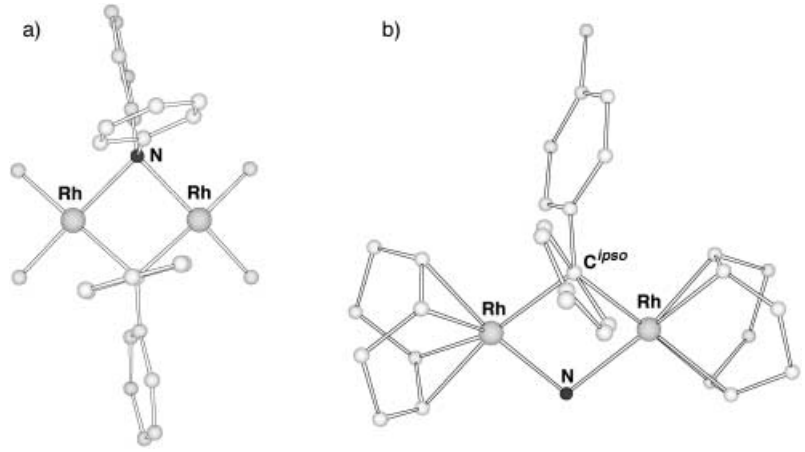


Figure 7. A partial view of the structures of the complexes **13** (a) and **5** (b) showing the disposition of the aromatic rings of the secondary amides.

with ^{1}H,^{1}H-COSY experiments, with the additional aid of the information provided by the structures found in the solid state. As all the complexes possess an element of symmetry that produces equivalence of the two "RhL_2" moieties, just one diolefin ligand is considered in the following discussion.

Complexes with secondary amides

These complexes with two identical substituents on the nitrogen atoms lack *syn*/*anti* isomers and are therefore best suited for the detection of conformational equilibria. Complexes **4** and **5** are fluxional, but on cooling to $-83\,^{\circ}$C their slow-exchange spectra are observed. The spectroscopic data obtained at this temperature indicate the presence of a single species with a structure similar to that found for **5** in the solid state, namely a planar conformation with restricted rotation of the aromatic rings leading to D_2 symmetry. Thus, the four aromatic rings give rise to four and five resonances in complexes **5** and **4**, respectively, which are all coupled in the ^{1}H,^{1}H-COSY spectra. Therefore, the four aromatic rings are equivalent, while the aromatic protons of the observed single ring are nonequivalent. This inequivalence of the protons indicates that there is no free rotation of the rings about the N–C^{ipso} bonds other than the slight movement required to achieve equivalence of the rings.

On heating, the signals of the cod and aromatic protons coalesce, and eventually they appear as three resonances due to the cod ligands and two (**5**) and three (**4**) resonances due to the aromatic protons at 75 °C. These high-temperature spectra are consistent with a planar conformation of the "RhN_2Rh" ring and free rotation of the aromatic rings to achieve the observed D_{2h} symmetry. Therefore, the fluxional process undergone by complexes **4** and **5** was identified as being due to rotation of the aromatic rings about the N–C^{ipso} bonds, which is restricted at low temperature and fully free at high temperature. For complex **5**, a plot of ln(k/T) versus 1/T led to the values $\Delta H^{\ddagger} = 50.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 0.79$ J mol^{-1} K^{-1}, and $\Delta G_{298}{}^{\ddagger} = 50.2$ kJ mol^{-1}. The near-zero value of $\Delta S^{\ddagger}$ is consistent with the intramolecular nature of the process. The $\Delta G_{298}{}^{\ddagger}$ value for complex **5** is about half of that found for the tris(μ-amido) complex [{(η^6-C_6Me_6)-Ru}$_2$(μ-NHPh)$_3$],[19] which is probably due to the greater steric encumbrance in the latter.

The related complex [{Rh(μ-NPh_2)(CN*t*Bu)$_2$}$_2$] (**13**) was also found to be fluxional, as indicated by the equivalence of the four phenyl rings in the room temperature ^{1}H NMR spectrum (see Experimental Section). This feature, and the observation of just a doublet for the eight *ortho* protons, indicated a planar conformation of the averaged species responsible for the spectrum, along with free rotation of the phenyl groups. To obtain such an averaged structure from the folded structure found in the solid state (Figure 5), free rotation of the phenyl groups about the N–C^{ipso} bonds with simultaneous inversion of the four-membered "RhN_2Rh" ring would be required. On cooling to $-90\,^{\circ}$C, only a broadening of the signals was detected. Therefore, the rotational and conformational equilibria should be processes with small activation energies in this case, since they are fast on the NMR time scale.

Complexes with primary amides

Figure 8 shows the types of cod protons in the three stereochemistries of the complexes distinguishable by NMR methods if rotamers are not considered, and Table 5 shows the

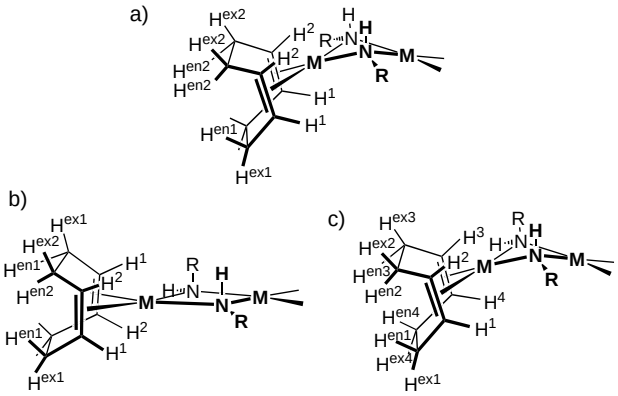


Figure 8. Types of cod protons for a) *syn* isomers, b) the *anti* planar isomer, and c) the *anti* folded isomer.

corresponding spectroscopic NMR features deduced from symmetry considerations. If the four-membered ring "RhN_2Rh" were rigid, the *syn* (folded and planar) isomers could be easily differentiated from the *anti* folded isomer on the basis of the number of signals due to the cod protons in the ^{1}H NMR spectra. In addition, the *syn* isomers may be differentiated from the *anti* planar form on the basis of the ^{1}H,^{1}H-COSY spectra, since the number of cross-peaks due to

  0947-6539/02/0814-3132 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 14

Table 5. Spectral features of [{M(μ-NHR)(cod)}$_2$] complexes.

Stereochemistry	Symmetry	R groups	Resonances of the cod protons	Cross-peaks for each methylenic proton
syn folded and planar	C_{2v}	equivalent	6	2
anti planar	C_{2h}	equivalent	6	4
anti folded	C_s	inequivalent	12	4

the methylene protons of the cod is distinct in each case. However, there is no easy way of distinguishing between the three *syn* conformers (Figure 1). Finally, the flexibility of these molecules may reduce the number of signals, and a detailed analysis of each particular case is required. For example, a fast inversion of the "RhN_2Rh" metallacycle of a folded *anti* isomer produces the spectrum expected for a rigid planar *anti* conformation.

The complexes containing the diolefin 1,5-cyclooctadiene [{M(μ-NHR)(cod)}$_2$] (M = Rh, R = Ph (**2**), 4-MeC_6H_4 (**3**); M = Ir, R = Ph (**9**), 4-MeC_6H_4 (**10**)) were found to exist as isomeric mixtures of two species in solution, the molar ratio being 2:3 for the rhodium derivatives and 1:1 for their iridium counterparts. These species were identified as the *syn* and *anti* isomers by analysis of the ^{1}H,^{1}H-COSY spectra (Table 5); the major rhodium species was the *syn* isomer. As an example, Figure 9 shows the ^{1}H,^{1}H-COSY spectrum of [{Rh(μ-4-HNC_6H_4Me)(cod)}$_2$] (**3**). Two cross-peaks are observed for each methylenic proton of the major species (*syn* isomer), while four cross-peaks are detected for these protons of the minor species (*anti* isomer in an averaged planar conformation). Moreover, the equivalence of the four *ortho* and four *meta* protons for both isomers indicates free rotation of the aromatic rings about the N–C^{ipso} bond at room temperature.

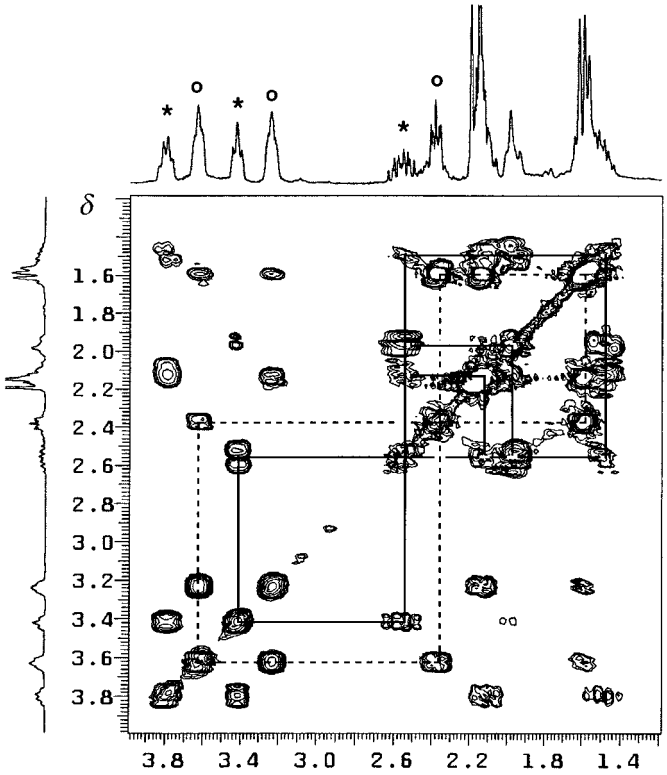


Figure 9. ^{1}H,^{1}H-COSY spectrum of [{Rh(μ-4-HNC_6H_4Me)(cod)}$_2$] (**3**) in the cod region. Selected cod resonances and correlations are indicated for the *syn* (o) and *anti* (*) isomers.

Freshly prepared solutions of complexes **3** and **10** at low temperature contain only the *syn*-[{M(μ-4-HNC_6H_4Me)(cod)}$_2$] isomers, that is, that found in the solid state for **3**. These isomers equilibrate to give the above mentioned mixtures of *syn*/*anti* isomers, the 2:3 and 1:1 molar ratios being attained in less than 1 h at room temperature.

No change in the molar ratios was seen on cooling the *syn*/*anti* mixtures of complexes **2**/**3** and **9**/**10**. While the aromatic resonances of *anti*-[{M(μ-NHR)(cod)}$_2$] were unaffected on cooling, those of the *syn*-[{M(μ-NHR)(cod)}$_2$] complexes were split into four and five signals at $-80\,^\circ$C. These signals were attributable to a single aromatic ring, as deduced from the ^{1}H,^{1}H-COSY spectra. Therefore, the rotation of the aromatic substituents is slowed down in the *syn* isomers at $-80\,^\circ$C, while it still remains for the *anti* isomers at this temperature. Moreover, the C_{2v} symmetry of the *syn* isomers was maintained since all cod resonances were unaffected at low temperature. This symmetry and the number of aromatic signals are only compatible with the rotamer-(0°) in a *syn*,*endo* or planar conformation. In particular, as activation parameters for the rotation of the aromatic rings about the N–C^{ipso} bond, values of $\Delta H^{\neq} = 41.0\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -1.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta G_{298}{}^{\neq} = 41.4\ \mathrm{kJ\,mol^{-1}}$ were obtained for the complex *syn*-[{Rh(μ-4-HNC_6H_4Me)(cod)}$_2$] (**3**) (Figure 10). The small value of $\Delta S^{\neq}$ and the lack of line-broadening effects upon dilution are consistent with the intramolecular nature of the process, while the activation energy ($\Delta G_{298}{}^{\neq}$) for *syn*-**3**, which is smaller than that for **5**, correlates well with the steric crowding of the molecules.

The complex incorporating the diolefin tfb, [{Rh(μ-4-HNC_6H_4Me)(tfb)}$_2$] (**8**), was found to exist as a single *syn* species in solution, in contrast to the cod analogues, and no isomerization to the *anti* species was observed on heating in [D_8]toluene.

To elucidate the possible influence of electronic factors on the *syn*,*anti* configurational preferences, we studied the isocyanide complexes [{Rh(μ-NHR)(CN*t*Bu)$_2$}$_2$] (R = Ph (**11**), 4-MeC_6H_4 (**12**)), which also allow comparison to be made with the analogous tetracarbonyl derivatives.[20] The room temperature ^{1}H NMR spectra of **11** and **12** are very simple, showing a singlet due to the four equivalent CN*t*Bu ligands, a singlet due to the NH protons, and either two (**12**) or three (**11**) resonances in the aromatic region. On cooling to $-80\,^\circ$C, the aromatic signals are split into four (**12**) and five (**11**), while the signal due to the CN*t*Bu ligands remains unchanged. Similar behavior was observed for the complexes [{M(μ-4-HNC_6H_4Me)$(CO)_2$}$_2$], which were specifically prepared for these studies. These changes indicate that the rotation of the aromatic rings, which is frozen at low temperature, is the motion responsible for the fluxionality of these complexes. However, the NMR data are insufficient

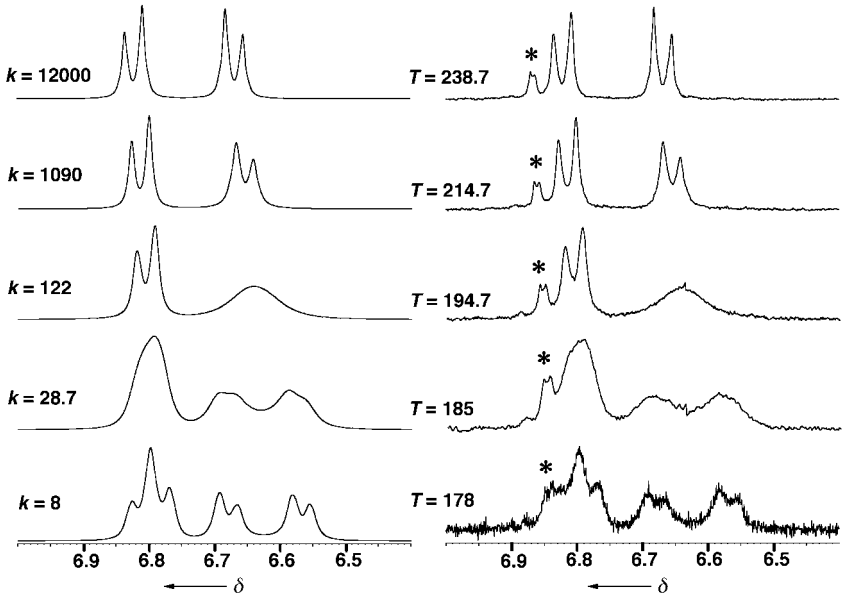


Figure 10. Experimental variable-temperature NMR spectra (right) in the region of the aromatic protons compared with the simulated spectra (left) for the rotation of the *p*-tolyl rings of *syn*-[{Rh(μ-4-HNC$_6$H$_4$Me)(cod)}$_2$] (**3**). The signal labeled * corresponds to the *anti* isomer.

to assign a *syn* or a planar *anti* configuration to complexes **11** and **12**, although they could well be the *syn*,*endo* isomers as found for **12** in the solid state. Moreover, configurational isomerizations were not detected for complexes **11**, **12**, or [{Rh(μ-4-HNC$_6$H$_4$Me)(CO)$_2$}$_2$].

The complex [{Rh(μ-NH*t*Bu)(cod)}$_2$] (**1**), with aliphatic and bulky amido ligands, represents a special case and was found to be non-fluxional. Its room temperature ^{1}H NMR spectrum shows nonequivalent *t*Bu groups and twelve resonances due to the cod protons, consistent with the *anti* isomer of a puckered conformation of the "RhN$_2$Rh" ring. Moreover, the *anti* conformation of the species in solution is clearly indicated by the coupling of each methylenic proton of the cod with four other protons. Furthermore, the "RhN$_2$Rh" ring remains folded and rigid, since weak line-broadening effects on the signals of the *t*Bu groups are only observed on heating in [D$_8$]toluene.

Discussion

The rarity and high reactivity of the known monodentate amido rhodium and iridium complexes in a low oxidation state prompted us to search for general methods for their synthesis. It is now clearly established that metathesis reactions of the lithium salts of primary and secondary amines with chloro complexes of the type [{M(μ-Cl)(diolefin)}$_2$] (M = Rh, Ir) afford a variety of diolefin rhodium and iridium complexes bridged by two simple organoamide ligands of the type [{M(μ-NRR′)(diolefin)}$_2$]. These reactions take place in a stepwise manner, with mixed-bridged complexes [{M(diolefin)}$_2$(μ-NRR′)(μ-Cl)] also being isolable. Overall, they provide a convenient entry to the organoamido chemistry of rhodium and iridium, even for complexes derived from aliphatic amines, which are almost unknown for the late transition metals.

The straightforward syntheses reported herein indicate that the supposed weakness[9] of the (amido)N–M(late transition metal) bond can be overcome, and stable compounds can be isolated. It has been suggested that the scarcity of late transition metal systems with π-donating ligands is due to a π-electron conflict between filled metal dπ orbitals and lone electron pairs residing on the π-donating ligands, which increases the reactivity of the metal–heteroatom moieties.[21] In the present case, the lack of lone electron pairs on the amido nitrogen in the dinuclear complexes might account for the differences in reactivity and stability when compared with mononuclear organoamido complexes. On the other hand, these compounds are still very reactive towards protic compounds such as water and alcohols, even when the latter are present as impurities in solvents, readily affording first the complexes [{M(diolefin)}$_2$(μ-NRR′)(μ-OR″)] (R″ = Me, H) and ultimately [{M(μ-OR″)(diolefin)}$_2$]. As for other dinuclear complexes, the replacement of the diolefin ligands by carbon monoxide or *tert*-butyl isocyanide takes place without disruption of the dinuclear entity to give the complexes [{M(μ-NRR′)(L)$_2$}$_2$].

In view of the paucity of available data, we have specifically addressed the structural and NMR properties of the bis(μ-amido) complexes reported herein. Our results provide insight into the configurations, conformations, and fluxionalities of these rhodium and iridium dinuclear compounds. The simplest case scenario corresponds to the complexes with secondary amides [{Rh(μ-NR$_2$)(cod)}$_2$] (**4**, **5**) and [{Rh(μ-NPh$_2$)(CN*t*Bu)$_2$}$_2$] (**13**), for which there is no possibility of *syn*/*anti* isomerism. While the diolefin complex **5** shows a nearly planar conformation of the "RhN$_2$Rh" metallacycle in the solid state, the analogous complex with *tert*-butyl isocyanide ligands (**13**) was found to be folded. The nearly planar conformation found for the cod complexes **4** and **5** is the most stable situation in terms of the avoidance of steric crowding effects arising from the contacts between the phenyl rings and the ancillary ligands. Accordingly, the fluxional behavior of **4** and **5** is limited to the rotation of the phenyl rings about the N–C^{ipso} bond, whereas complex **13**, which is not subject to steric crowding effects, undergoes both movements, namely rotation of the rings and inversion of the metallacycle.

In solution, the dinuclear bis(μ-amido) complexes with primary amides were found to exist either as a single *syn* or *anti* isomer or, in some instances, as a mixture of both isomers in equilibrium. In particular, the complexes [{M(μ-NHR)(L$_2$)}$_2$] (R = Ph, 4-MeC$_6$H$_4$) with sterically undemand-

  0947-6539/02/0814-3134 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 14

ing ancillary ligands (tfb, CO, CN*t*Bu) were found to adopt the *syn* configuration. These do not isomerize to the *anti* isomer even on heating, which suggests that the thermodynamically most stable configuration for these complexes is *syn*. Accordingly, the incorporation of the bulkier diolefin cod produced important differences. Thus, the compounds [{M(μ-NHR)(cod)}$_2$] (M = Rh, Ir; R = Ph, 4-MeC_6H_4) adopt the *syn* configuration in the solid state, but readily equilibrate to *syn*/*anti* mixtures in solution. The preference for the *anti* configuration on increasing the bulkiness of the ancillary and bridging ligands would seem to be plausible, considering that the complex with bulkiest ligands [{Rh(μ-NH*t*Bu)(cod)}$_2$] (**1**) shows the *anti* configuration. Moreover, no isomerization of *anti*-**1** to *syn*-**1** was observed. These results indicate a close relationship between the *anti* configuration and minimization of the contacts between the bridging and ancillary ligands.

Having established the *syn* versus *anti* configurational preferences, we turned our attention to the conformations, folded versus planar, as well as to the fluxional processes undergone by both isomers. The two *syn* isomers characterized by X-ray methods, [{Rh(μ-4-HNC_6H_4Me)(cod)}$_2$] (**3**) and [{Rh(μ-4-HNC_6H_4Me)(CN*t*Bu)$_2$}$_2$] (**12**), were found to exist as rotamer-(0°) of the folded *syn*,*endo* conformers in the solid state. The rotamer-(0°) form of the *syn*,*endo* conformers is probably favored by the close proximity of the ancillary ligands and the aromatic rings. This is also the most probable stereochemistry of the species in solution at low temperature. In support of this statement, note that the inversion of the "RhN_2Rh" metallacycle in all the *syn* isomers (Figure 11)

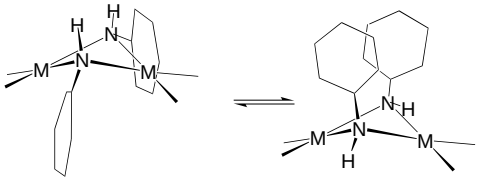


Figure 11. Inversion of the "RhN_2Rh" metallacycle in the *syn* isomers.

requires the simultaneous rotation of the aromatic rings to avoid contact between them. Since only the rotamer-(0°) is observed by NMR spectroscopy at low temperature, indicating that the rotation of the aromatic rings is frozen for the *syn* isomers, the inversion of the "RhN_2Rh" metallacycle is also slowed down. On heating, inversion of the "RhN_2Rh" ring becomes operative in the *syn* configurations, since free rotation of the aromatic rings with a small activation energy is observed.

The *anti* isomers with aromatic amides were found to be species having a planar conformation with free rotation of the aromatic rings in solution. Their fluxional behavior could not be slowed down at low temperature, which indicates that the processes have lower activation energies than those for the *syn* analogues. Assuming that these isomers are folded, the inversion of the metallacycle should be fast on the NMR time scale so as to produce an averaged planar conformation. The smaller activation energies for inversion of the metallacycle and rotation of the aromatic rings for the *anti* isomers can be explained on the basis of their stereochemistries. An aromatic ring in the equatorial position in a folded *anti* isomer (Figure 12) has an identical environment to that observed for the *syn* isomers, and thus can be expected to show similar rotational behavior, while the axial aromatic ring can rotate freely. Moreover, inversion of the "RhN_2Rh" ring seems to be

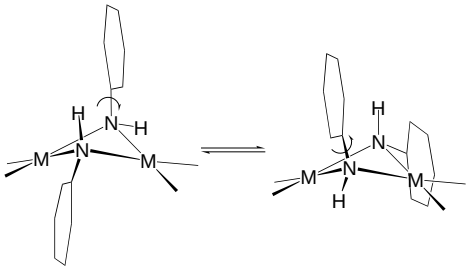


Figure 12. Inversion of the "RhN_2Rh" metallacycle in the *anti* isomers.

an easy motion when the two aromatic rings are coplanar. Consequently, with these processes acting in tandem, the required motion is easier than in the case of their *syn* counterparts. This intuitive idea would account for the fluxionality shown by the *anti*-[{M(μ-NHR)(cod)}$_2$] (M = Rh, Ir; R = Ph, 4-MeC_6H_4) compounds over the temperature range studied.

Finally, the complex [{Rh(μ-NH*t*Bu)(cod)}$_2$] (**1**) was found to be a static *anti*-folded isomer. In this case, the presence of the bulky *t*Bu groups not only favors an *anti* stereochemistry, but also prevents the complex from achieving the planar conformation needed to undergo inversion of the "RhN_2Rh" ring.

Experimental Section

Starting materials and physical methods: All reactions were carried out under argon using standard Schlenk techniques. [{M(μ-Cl)(cod)}$_2$][22] was prepared according to literature methods and recrystallized from dichloromethane/hexane. *p*-Toluidine, diphenylamine, and bis(*p*-tolyl)amine were sublimed prior to use; aniline and *tert*-butylamine were purified by distillation. *n*BuLi (1.6 M in hexane) was purchased from Fluka and was titrated before use. Solvents were dried by standard methods and distilled under argon before use. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. Ions were produced with the standard Cs^+ gun at about 30 kV and 3-nitrobenzyl alcohol (NBA) was used as the matrix. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker ARX 300 and Varian UNITY 300 spectrometers operating at 299.95 and 300.13 MHz, respectively, for ^{1}H. Chemical shifts are reported in parts per million downfield from $SiMe_4$ ($\delta = 0$) using the residual signal of the deuterated solvent as a reference.

Preparation of the omplexes

[{Rh(μ-NH*t*Bu)(cod)}$_2$] (1): A solution of *n*BuLi (400.0 μL, 0.69 mmol) in hexanes was added dropwise to a solution of *t*BuNH_2 (72.5 μL, 0.69 mmol) in diethyl ether (10 mL). After stirring for 1 h at room temperature, solid [{Rh(μ-Cl)(cod)}$_2$] (113.4 mg, 0.23 mmol) was added, which led to the slow precipitation of an orange solid. Stirring was continued for 18 h and then the mixture was concentrated to dryness. The orange residue was washed with methanol (2 × 15 mL) at −78 °C and with hexane (2 × 5 mL) at room temperature, and then dried in vacuo. Yield: 97.7 mg (75 %); elemental analysis calcd (%) for $C_{24}H_{44}N_2Rh_2$ (566.4): C 50.89, H 7.83, N 4.95; found: C 50.95, H 7.43, N 5.05; ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 4.95$ (m, 2H;

=CH), 4.42 (m, 2H; =CH), 4.03 (m, 2H; =CH), 3.20 (m, 2H; =CH), 2.65 (m, 2H; CH_2^{exo}), 2.40 (m, 2H; CH_2^{exo}), 2.30 (m, 4H; CH_2^{exo}), 1.90 (m, 4H; CH_2^{endo}), 1.68 (m, 4H; CH_2^{endo}), 1.31 (s, 9H; *t*Bu), 1.11 (s, 9H; *t*Bu), 1.59 (s, 1H; NH), 0.60 (s, 1H; NH); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): $\delta = 77.2$ (d, $^1J(C,Rh) = 12$ Hz; =CH), 77.1 (d, $^1J(C,Rh) = 13$ Hz; =CH), 75.3 (d, $^1J(C,Rh) = 11$ Hz; =CH), 72.1 (d, $^1J(C,Rh) = 12$ Hz; =CH), 56.6 ($C(CH_3)_3$), 56.4 ($C(CH_3)_3$), 37.7 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 32.7 (CH_2), 32.1 (CH_2), 30.7 (CH_2), 30.0 (CH_2); MS: *m*/*z* (%): 566 (37) [M^+], 494 (100) [$M^+ - t$BuNH].

[{Rh(μ-NHPh)(cod)}$_2$] (2): *n*BuLi (1.20 mL, 2.06 mmol) was added to a solution of freshly distilled aniline (182.2 μL, 2.06 mmol) in diethyl ether (10 mL), resulting in the precipitation of a white solid. After stirring for 15 min, the suspension obtained was cooled to −40 °C and solid [{Rh(μ-Cl)(cod)}$_2$] (508.0 mg, 1.03 mmol) was added, which led to the immediate precipitation of a yellow microcrystalline solid. After stirring for 2 h at −40 °C, the mixture was allowed to warm to room temperature and stirring was continued for a further 1 h. The resulting suspension was concentrated to dryness in vacuo and the residue was washed with acetone/water (1:1; 2 × 15 mL) at −78 °C and with cold acetone (3 mL), and then dried in vacuo. Yield: 575.7 mg (92%), elemental analysis calcd (%) for $C_{28}H_{36}N_2Rh_2$ (606.4): C 55.46, H 5.98, N 4.62; found: C 55.29, H 6.55, N 4.52; ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 7.06$ (m; Ph), 6.87 (d, $^3J(H,H) = 8.4$ Hz; Ph), 6.75 (t, $^3J(H,H) = 8.4$ Hz; Ph); for the *anti* isomer (40%): 3.97 (m, 4H; =CH), 3.51 (m, 4H; =CH), 2.38 (m, 4H; CH_2^{exo}), 1.98 (m, 4H; CH_2^{exo}), 1.80 (m, 4H; CH_2^{endo}), 1.32 (m, 4H; CH_2^{endo}), 1.27 (s, 2H; NH); for the *syn* isomer (60%): 3.83 (m, 4H; =CH), 3.48 (m, 4H; =CH), 2.30 (m, 4H; CH_2^{exo}), 2.04 (m, 4H; CH_2^{exo}), 1.47 (m, 8H; CH_2^{endo}), 2.10 (s, 2H; NH). $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): $\delta = 155.1$, 154.2, 128.9, 128.1, 126.7, 122.1, 121.6, 120.1 (Ph); for the *anti* isomer: 79.8 (d, $^1J(C,Rh) = 12$ Hz; =CH), 77.6 (d, $^1J(C,Rh) = 13$ Hz; =CH), 32.3 (CH_2), 29.3 (CH_2); for the *syn* isomer: 79.0 (d, $^1J(C,Rh) = 13$ Hz; =CH), 76.9 (d, $^1J(C,Rh) = 13$ Hz; =CH), 30.7 (CH_2), 30.0 (CH_2).

[{Rh(μ-4-HNC$_6$H$_4$Me)(cod)}$_2$] (3): This compound was prepared as described for **2** starting from *p*-toluidine (379.3 mg, 3.54 mmol), *n*BuLi (2.00 mL, 3.54 mmol), and [{Rh(μ-Cl)(cod)}$_2$] (872.8 mg, 1.77 mmol). Yield: 1055.6 mg (94%); elemental analysis calcd (%) for $C_{30}H_{40}N_2Rh_2$ (634.5): C 56.79, H 6.35, N 4.42; found: C 56.74, H 6.00, N 4.38; ^{1}H NMR (CD_2Cl_2, 25 °C) for the *anti* isomer (40%): $\delta = 6.87$ (m, 8H; *p*-MeC$_6H_4$), 3.81 (m, 4H; =CH), 3.43 (m, 4H; =CH), 2.59 (m, 4H; CH_2^{exo}), 1.99 (m, 4H; CH_2^{exo} cod), 2.17 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.53 (m, 4H; CH_2^{endo}), 1.51 (m, 4H; CH_2^{endo}), 1.93 (s, 2H; NH); for the *syn* isomer (60%): $\delta = 6.83$ (δ_A, 4H), 6.68 (δ_B, J(A,B) = 8.1 Hz, 4H; *p*-MeC$_6H_4$), 3.63 (m, 4H; =CH), 3.24 (m, 4H; =CH cod), 2.43 (m, 4H; CH_2^{exo}), 1.99 (m, 4H; CH_2^{exo}), 2.15 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.53 (m, 8H; CH_2^{endo}), 1.48 (s, 2H; NH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C) for the *anti* isomer: $\delta = 153.7$, 130.9, 130.5, 123.0 (*p*-MeC$_6$H$_4$); 81.9 (d, $^1J(C,Rh) = 12$ Hz; =CH), 78.5 (d, $^1J(C,Rh) = 13$ Hz; =CH), 34.7 (CH_2), 30.6 (CH_2), 22.3 (*p*-*Me*C$_6$H$_4$); for the *syn* isomer: $\delta = 152.3$, 130.8, 130.2, 123.4 (*p*-MeC$_6$H$_4$); 81.0 (d, $^1J(C,Rh) = 13$ Hz; =CH), 77.5 (d, $^1J(C,Rh) = 13$ Hz; =CH), 32.4 (CH_2), 31.7 (CH_2), 22.3 (*p*-*Me*C$_6$H$_4$); MS: *m*/*z* (%): 634 (30) [M^+], 528 (100) [M^+ − 4-MeC$_6$H$_4$NH].

[{Rh(μ-NPh$_2$)(cod)}$_2$] (4): This compound was prepared as described for **2** starting from Ph$_2$NH (228.8 mg, 1.35 mmol), *n*BuLi (800.0 μL, 1.35 mmol), and [{Rh(μ-Cl)(cod)}$_2$] (335.3 mg, 0.68 mmol). After concentration of the reaction mixture to dryness, the residue was washed with methanol (3 × 10 mL) at −78 °C and with hexane (2 × 5 mL) at room temperature, and then dried in vacuo. Yield: 461.0 mg (90%); elemental analysis calcd (%) for $C_{40}H_{44}N_2Rh_2$ (758.6): C 63.33, H 5.85, N 3.69; found: C 63.33, H 6.03, N 3.56; ^{1}H NMR ($CDCl_3$, −55 °C): $\delta = 9.98$ (d, $^3J(H,H) = 8.1$ Hz, 4H; H^{o1}), 7.63 (m, 4H; H^{m1}), 6.93 (m, 8H; H^p+H^{m2}), 6.73 (br s, 4H; H^{o2}), 2.87 (m, 4H; =CH), 2.68 (m, 4H; =CH), 2.51 (m, 4H; CH_2^{exo}), 1.73 (m, 4H; CH_2^{exo}), 1.63 (m, 4H; CH_2^{endo}), 0.96 (m, 4H; CH_2^{endo}).

[{Rh[μ-N(4-MeC$_6$H$_4$)$_2$](cod)}$_2$] (5): This compound was prepared as described for **2** starting from *N*,*N*-bis(*p*-tolyl)amine (165.7 mg, 0.84 mmol), *n*BuLi (500.0 μL, 0.84 mmol), and [{Rh(μ-Cl)(cod)}$_2$] (207.1 mg, 0.42 mmol). Yield: 305.0 mg (89%); elemental analysis calcd (%) for $C_{44}H_{52}N_2Rh_2$ (814.7): C 64.86, H 6.43, N 3.43; found: C 64.33, H 6.03, N 3.56; ^{1}H NMR ([D$_8$]toluene, −70 °C): $\delta = 10.37$ (δ_A, 4H), 7.61 (δ_B, J(A,B) = 9.1 Hz, 4H; *p*-MeC$_6H_4$), 7.03 (δ_A, 4H), 6.83 (δ_B, J(A,B) = 9.1 Hz, 4H; *p*-MeC$_6H_4$), 3.27 (m, 4H; =CH), 3.18 (m, 4H; =CH), 2.68 (m, 4H; CH_2^{exo}), 1.58 (m, 4H; CH_2^{exo}), 2.34 (s, 12H; *p*-*Me*C$_6$H$_4$), 1.23 (m, 4H; CH_2^{endo}), 0.61 (m, 4H; CH_2^{endo}).

[{Rh(cod)}$_2$(μ-NH*t*Bu)(μ-Cl)] (6): This compound was prepared as described for **1** starting from *t*BuNH$_2$ (54.8 μL, 0.51 mmol), *n*BuLi (300.0 μL, 0.51 mmol), and [{Rh(μ-Cl)(cod)}$_2$] (251.5 mg, 0.51 mmol). Yield: 185.0 mg (73%); elemental analysis calcd. (%) for $C_{20}H_{34}NClRh_2$ (529.8): C 45.34, H 6.46, N 2.64; found: C 45.36, H 6.42, N 2.33; ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 4.72$ (m, 2H; =CH), 4.35 (m, 2H; =CH), 3.83 (m, 2H; =CH), 3.21 (m, 2H; =CH), 2.43 (m, 2H; CH_2^{exo}), 2.30 (m, 4H; CH_2^{exo}), 2.15 (m, 2H; CH_2^{exo}), 1.73 (m, 4H; CH_2^{endo}), 1.62 (m, 4H; CH_2^{endo}), 1.42 (s, 9H; *t*Bu), 1.21 (s, 1H; NH); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): $\delta = 83.8$ (d, $^1J(C,Rh) = 11$ Hz; =CH), 82.2 (d, $^1J(C,Rh) = 11$ Hz; =CH), 74.4 (d, $^1J(C,Rh) = 17$ Hz; =CH), 70.2 (d, $^1J(C,Rh) = 16$ Hz; =CH), 58.2 ($C(CH_3)_3$), 36.8 ($C(CH_3)_3$), 32.4 (CH_2), 32.0 (CH_2), 30.7 (CH_2), 29.8 (CH_2); MS: *m*/*z* (%): 529 (100) [M^+], 494 (30) [M^+ − Cl].

[{Rh(cod)}$_2$(μ-4-HNC$_6$H$_4$Me)(μ-Cl)] (7): This compound was prepared as described for **2** starting from *p*-toluidine (34.7 mg, 0.32 mmol), *n*BuLi (200.0 μL, 0.32 mmol), and [{Rh(μ-Cl)(cod)}$_2$] (159.8 mg, 0.32 mmol). Yield: 158.3 mg (87%); elemental analysis calcd. (%) for $C_{23}H_{32}NClRh_2$ (563.8): C 49.00, H 5.72, N 2.48; found: C 49.06, H 5.72, N 2.66; ^{1}H NMR (CD_2Cl_2, 25 °C): $\delta = 6.82$ (m, 4H; *p*-MeC$_6H_4$), 4.27 (m, 2H; =CH), 2.15 (m, 2H; =CH), 3.66 (m, 2H; =CH), 3.39 (m, 2H; =CH), 2.46 (m, 4H; CH_2^{exo}), 2.39 (m, 2H; CH_2^{exo}), 2.35 (m, 2H; CH_2^{exo}), 2.16 (s, 3H; *p*-*Me*C$_6$H$_4$), 1.90 (m, 2H; CH_2^{endo}), 1.78 (m, 4H; CH_2^{endo}), 1.60 (m, 2H; CH_2^{endo}), 1.25 (s, 1H; NH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): $\delta = 152.4$, 131.6, 130.9, 123.4 (*p*-MeC$_6$H$_4$); 83.9 (d, $^1J(C,Rh) = 11$ Hz; =CH), 83.6 (d, $^1J(C,Rh) = 11$ Hz; =CH), 78.1 (d, $^1J(C,Rh) = 16$ Hz; =CH), 76.7 (d, $^1J(C,Rh) = 16$ Hz; =CH), 33.8 (CH_2), 32.8 (CH_2), 32.5 (CH_2), 31.8 (CH_2), 22.2 (*p*-*Me*C$_6$H$_4$).

[{Rh(μ-4-HNC$_6$H$_4$Me)(tfb)}$_2$] (8): This compound was prepared as described for **2** starting from *p*-toluidine (116.8 mg, 1.09 mmol), *n*BuLi (1.00 mL, 1.09 mmol), and [{Rh(μ-Cl)(tfb)}$_2$] (393.7 mg, 0.54 mmol). Yield: 390.0 mg (83%); elemental analysis calcd (%) for $C_{38}H_{28}N_2F_8Rh_2$ (870.5): C 52.43, H 3.24, N 3.22; found: C 52.12, H 3.85, N 3.13; ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 6.85$ (δ_A, 4H), 6.51 (δ_B, J(A,B) = 8.2 Hz, 4H; *p*-MeC$_6H_4$), 5.25 (m, 2H; CH), 4.91 (m, 2H; CH), 3.11 (m, 4H; =CH), 2.60 (m, 4H; =CH), 2.10 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.24 (s, 2H; NH); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): $\delta = 152.0$ (C^i), 128.8 (C^p), 128.7 (C^m), 120.5 (C^o), 56.3 (d, $^1J(C,Rh) = 11$ Hz; =CH), 53.0 (d, $^1J(C,Rh) = 11$ Hz; =CH), 40.2 (CH), 39.6 (CH), 20.3 (*p*-*Me*C$_6$H$_4$); MS: *m*/*z* (%): 870 (90) [M^+], 763 (100) [M^+ − 4-MeC$_6$H$_4$NH].

[{Ir(μ-NHPh)(cod)}$_2$] (9): This compound was prepared as described for **2** starting from PhNH$_2$ (68.8 μL, 0.75 mmol), *n*BuLi (700.0 μL, 0.75 mmol), and [{Ir(μ-Cl)(cod)}$_2$] (248.5 mg, 0.37 mmol). Yield: 194.6 mg (67%); elemental analysis calcd (%) for $C_{28}H_{36}N_2Ir_2$ (785.0): C 42.84, H 4.62, N 3.57; found: C 43.39, H 4.03, N 3.66; ^{1}H NMR ([D$_6$]benzene, 25 °C): $\delta = 7.12$ (t, $^3J(H,H) = 7.2$ Hz, 2H; H^mPh^1), 7.06 (d, $^3J(H,H) = 7.2$ Hz, 2H; H^oPh^1), 6.80 (t, $^3J(H,H) = 7.2$ Hz, 1H; H^pPh^1), 7.04 (t, $^3J(H,H) = 7.2$ Hz, 2H; H^mPh^2), 6.89 (d, $^3J(H,H) = 7.2$ Hz, 2H; H^oPh^2), 6.76 (t, $^3J(H,H) = 7.2$ Hz, 1H; H^pPh^2), 3.95 (s, 1H; NH), 2.36 (s, 1H; NH); for the *anti* isomer (50%): 3.98 (m, 4H; =CH), 3.46 (m, 4H; =CH), 2.25 (m, 4H; CH_2^{exo}), 2.05 (m, 4H; CH_2^{exo}), 1.87 (m, 4H; CH_2^{endo}), 1.29 (m, 4H; CH_2^{endo}); for the *syn* isomer (50%): 3.87 (m, 4H; =CH), 3.36 (m, 4H; =CH), 2.27 (m, 4H; CH_2^{exo}), 2.01 (m, 4H; CH_2^{exo}), 1.41 (m, 8H; CH_2^{endo}); $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): $\delta = 152.1$, 150.1, 128.1, 128.0, 123.4, 122.6, 122.4, 122.2 (Ph); 63.8, 63.1, 60.6, 60.3 (=CH); 34.0, 31.9, 31.1, 30.6 (CH_2); MS: *m*/*z* (%): 785 (65) [M^+].

[{Ir(μ-4-HNC$_6$H$_4$Me)(cod)}$_2$] (10): This compound was prepared as described for **2** starting from *p*-toluidine (79.3 mg, 0.74 mmol), *n*BuLi (700.0 μL, 0.74 mmol), and [{Ir(μ-Cl)(cod)}$_2$] (248.5 mg, 0.37 mmol). Yield: 250.0 mg (83%); elemental analysis calcd (%) for $C_{30}H_{40}N_2Ir_2$ (813.1): C 44.32, H 4.96, N 3.44; found: C 44.70, H 4.68, N 3.07; ^{1}H NMR (CD_2Cl_2, 25 °C): for the *anti* isomer (50%) $\delta = 6.96$ (m, 8H; *p*-MeC$_6H_4$), 3.87 (s, 2H; NH), 3.81 (m, 4H; =CH), 3.37 (m, 4H; =CH), 2.35 (m, 4H; CH_2^{exo}), 2.06 (m, 4H; CH_2^{exo}), 2.26 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.92 (m, 4H; CH_2^{endo}), 1.29 (m, 4H; CH_2^{endo}); for the *syn* isomer (50%): $\delta = 6.97$ (δ_A, 4H), 6.76 (δ_B, J(A,B) = 7.8 Hz, 4H; *p*-MeC$_6H_4$), 3.64 (m, 4H; =CH), 3.13 (m, 4H; =CH), 2.70 (s, 2H; NH), 2.25 (m, 4H; CH_2^{exo}), 1.98 (m, 4H; CH_2^{exo}), 2.26 (s, 6H; *p*-*Me*C$_6$H$_4$), 1.43 (m, 8H; CH_2^{endo}); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): $\delta = 149.5$ (C^i), 147.5 (C^i), 131.6 (C^p), 131.5 (C^p), 129.2 (C^m), 128.4 (C^m), 122.9 (C^o), 122.3 (C^o), 63.9, 63.3, 60.5, 59.9 (=CH); 34.1, 31.7, 30.9, 30.3 (CH_2); 20.6, 20.5 (*p*-*Me*C$_6$H$_4$); MS: *m*/*z* (%): 813 (70) [M^+].

[{Rh(μ-NHPh)(CN*t*Bu)$_2$}$_2$] (11): *tert*-Butyl isocyanide (232.5 μL, 2.08 mmol) was slowly added to a suspension of [{Rh(μ-NHPh)(cod)}$_2$]

0947-6539/02/0814-3136 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 14

(**2**; 318.0 mg, 0.52 mmol) in diethyl ether (10 mL). After stirring for 4 h, the suspension obtained was concentrated to a volume of about 5 mL and hexane (10 mL) was added to complete the crystallization. The yellow microcrystalline solid was collected by filtration under argon, washed with hexane (2 × 5 mL), and dried in vacuo. Yield: 270.3 mg (69 %); elemental analysis calcd (%) for $C_{32}H_{48}N_6Rh_2$ (722.6): C 53.19, H 6.69, N 11.63; found: C 53.13, H 6.21, N 12.07; IR (diethyl ether): $\tilde{\nu}$ = 2123 (s), 2087 (m), 2054 (s) cm^{-1} (CN); ^{1}H NMR ([D$_6$]benzene, 25 °C): δ = 7.48 (d, ^3J(H,H) = 7.5 Hz, 4H; H^o), 7.11 (t, ^3J(H,H) = 7.5 Hz, 4H; H^m), 6.71 (t, ^3J(H,H) = 7.5 Hz, 2H; H^p), 2.49 (s, 2H; NH); 0.89 (s, 36H; *t*Bu); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): δ = 165.6 (C^i), 127.3 (C^m), 122.6 (C^o), 117.0 (C^p), 153.6 (d, ^1J(C,Rh) = 67 Hz; *C*NC(CH$_3$)$_3$), 127.3 (C^m), 54.9 (*C*(CH$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$); MS: *m*/*z* (%): 722 (25) [M^+].

[{Rh(μ-4-HNC$_6$H$_4$Me)(CN*t*Bu)$_2$}$_2$] (12): This compound was prepared as described for **11** starting from [{Rh(μ-4-HNC$_6$H$_4$Me)(cod)}$_2$] (**3**; 429.0 mg, 0.68 mmol) and *tert*-butyl isocyanide (300 μL, 2.70 mmol). Yield: 405.0 mg (80 %); elemental analysis calcd (%) for $C_{34}H_{52}N_6Rh_2$ (750.6): C 54.40, H 6.98, N 11.19; found: C 55.10, H 7.16, N 10.44; IR (cyclohexane): $\tilde{\nu}$ = 2131 (m), 2122 (s), 2091 (m), 2051 cm^{-1} (s; CN); ^{1}H NMR ([D$_6$]benzene, 25 °C): δ = 7.39 (δ_A, 4H), 6.91 (δ_B, J(A,B) = 8.1 Hz, 4H; *p*-MeC$_6$*H*$_4$), 2.43 (s, 2H; NH), 2.26 (s, 6H; *p*-*Me*C$_6$H$_4$), 0.92 (s, 36H; *t*Bu); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): δ = 162.8 (C^i), 127.8 (C^m), 125.2 (C^o), 122.4 (C^p), 54.8 (*C*(CH$_3$)$_3$), 30.5 (C(*C*H$_3$)$_3$), 20.7 (*p*-*Me*C$_6$H$_4$); MS: *m*/*z* (%): 750 (45) [M^+].

[{Rh(μ-NPh$_2$)(CN*t*Bu)$_2$}$_2$] (13): This compound was prepared as described for **11** starting from [{Rh(μ-NPh$_2$)(cod)}$_2$] (**4**; 380.0 mg, 0.50 mmol) and *tert*-butyl isocyanide (222.0 μL, 2.00 mmol). Yield: 284.0 mg (65 %); elemental analysis calcd (%) for $C_{44}H_{56}N_6Rh_2$ (874.8): C 60.41, H 6.45, N 9.61; found: C 60.27, H 6.40, N 9.81; IR (cyclohexane): $\tilde{\nu}$ = 2129 (s), 2104 (m), 2064 (s), 2056 cm^{-1} (s; CN); ^{1}H NMR ([D$_6$]benzene, 25 °C): δ = 8.32 (d, ^3J(H,H) = 7.8 Hz, 8H; H^o), 7.11 (t, ^3J(H,H) = 7.5 Hz, 8H; H^m), 6.80 (t, ^3J(H,H) = 7.2 Hz, 4H; H^p), 0.82 (s, 36H; *t*Bu); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): δ = 163.1 (C^i), 128.4 (C^m), 126.9 (C^o), 119.8 (C^p), 150.0 (d, ^1J(C,Rh) = 71 Hz; *C*NC(CH$_3$)$_3$), 55.1 (*C*(CH$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$); MS: *m*/*z* (%): 874 (25) [M^+], 706 (100) [$M^+ - 2$ CN*t*Bu].

Crystal structure determinations of compounds 3·C$_4$H$_{10}$O, 5, 12·1/2(C$_4$H$_{10}$O), and 13: A summary of crystal data and refinement parameters is given in Table 6. Data were collected at 173(2) K on a Siemens Smart APEX diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) using narrow ω scans (0.3°). Corrections for Lorentz and polarization effects were applied, and a multiscan absorption correction based on the multiplicity of the collected data was performed.[23] The structures were solved by the Patterson method (SHELXS97)[24] and difference Fourier techniques, and were refined by full-matrix least-squares on F^2 (SHELXL97).[24] Scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

All non-hydrogen atoms not involved in disorders were refined with anisotropic displacement parameters; the solvent molecules of **3** and **12**, and three *tert*-butyl groups of **13** were found to be disordered, and were refined with isotropic displacement parameters and restraints in their geometries. The positions of the hydrogen atoms were calculated, except for the hydrogens of the sp^2 carbon or nitrogen atoms bonded to the metals, which were located in difference-Fourier maps, and were refined as riding on the corresponding carbon or nitrogen atoms. The hydrogen atoms of the disordered solvent molecules (**3**, **12**) and of the *tert*-butyl groups of compound **13** were not included in the refinement. CCDC-177868–177871 (**3**, **5**, **12**, and **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 6. Crystallographic data for compounds **3**·C$_4$H$_{10}$O, **5**, **12**·1/2(C$_4$H$_{10}$O), and **13**.

	3·C$_4$H$_{10}$O	**5**	**12**·1/2(C$_4$H$_{10}$O)	**13**
chem. formula	$C_{34}H_{50}N_2ORh_2$	$C_{44}H_{52}N_2Rh_2$	$C_{36}H_{57}N_6O_{0.5}Rh_2$	$C_{44}H_{56}N_6Rh_2$
fw	708.58	814.70	787.70	874.77
crystal system	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$Pbcn$ (no. 60)	$P\bar{1}$ (no. 2)	$P2_1$/n (no. 14)
a [Å]	9.9100(10)	13.256(4)	11.3137(11)	14.001(3)
b [Å]	14.2145(14)	14.197(5)	12.7836(12)	19.261(4)
c [Å]	22.961(2)	19.454(6)	13.6555(13)	16.029(3)
α [°]	–	–	83.468(2)	–
β [°]	91.217(2)	–	86.671(2)	90.662(4)
γ [°]	–	–	84.791(2)	–
V [Å^3]	3233.7(6)	3661(2)	1951.8(3)	4322.1(15)
Z	4	4	2	4
ρ_{calcd} [g cm^{-3}]	1.455	1.478	1.340	1.344
μ(Mo$_{K\alpha}$) [mm^{-1}]	1.048	0.935	0.877	0.799
min./max. transmission	0.629/0.930	0.598/0.919	0.677/0.914	0.627/0.950
F(000)	1464	1680	818	1808
crystal size [mm]	0.10 × 0.14 × 0.24	0.10 × 0.11 × 0.13	0.06 × 0.08 × 0.28	0.05 × 0.06 × 0.11
θ range [°]	1.69–25.00	2.09–25.00	1.50–27.00	1.65–25.00
reflections collected	17264	18884	19007	23214
independent reflections	5675	3225	8411	7581
R_{int}	0.1002	0.1559	0.0661	0.1367
reflections [$F^2 > 2\sigma(F^2)$]	3585	1893	5321	3102
data/restraints/parameters	5675/22/365	3225/0/223	8411/7/414	7581/306/464
$R(F)$ [$F^2 > 2\sigma(F^2)$]	0.0530	0.0536	0.0516	0.0631
$wR(F^2)$ (all data)	0.1132	0.1151	0.1074	0.1510
GOF(F^2) (all data)	0.870	0.868	0.883	0.783
largest diff. peak/hole [e Å^{-3}]	0.733/−0.544	1.309/−0.883	1.314/−0.661	1.328/−0.786

Acknowledgements

Generous financial support from the Dirección General de Enseñanza Superior e Investigación (DGES) and the Ministerio de Ciencia y Tecnología (MCyT-PNI) (Projects PB98–641 and BQU2000–1170) is gratefully acknowledged.

[1] M. D. Fryzuk, W. R. Piers, *Organometallics* **1990**, *9*, 986.
[2] a) B. R. James, *Catalysis Today* **1997**, *37*, 209; b) R. Sablong, J. A. Osborn, J. W. Faller, *J. Organomet. Chem.* **1997**, *525*, 65; c) B. R. James, *Chem. Ind.* **1995**, *62*, 167; d) G. E. Ball, W. R. Cullen, M. D. Fryzuk, W. J. Henderson, B. R. James, K. S. MacFarlane, *Inorg. Chem.* **1994**, *33*, 1464, e) A. G. Becalski, W. R. Cullen, M. D. Fryzuk, B. R. James, G.-J. Kang, S. J. Rettig, *Inorg. Chem.* **1991**, *30*, 5002; f) J. Bakos, A. Orosz, B. Heil, M. Laghmari, P. Lhoste, D. Sinou, *J. Chem. Soc. Chem. Commun.* **1991**, 1684; g) T. Ng Cheong Chan, J. A. Osborn, *J. Am. Chem. Soc.* **1990**, *112*, 9400; h) F. Spindler, B. Pugin, H. U. Blaser, *Angew. Chem.* **1990**, *102*, 561; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 558; i) C. J. Longley, T. J. Goodwin, G. Wilkinson, *Polyhedron* **1986**, *5*, 1625.
[3] M. D. Fryzuk, W. E. Piers, S. J. Rettig, *Can. J. Chem.* **1992**, *70*, 2381.
[4] a) J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158; b) B. H. Yang, S. L. Buchwald, *J. Organomet. Chem.* **1999**, *576*, 125; c) F. E. Goodson, S. I. Hauck, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 7527; d) J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcázar-Román, *J. Org. Chem.* **1999**,

64, 5575; e) J. F. Hartwig, *Angew. Chem.* **1998**, *110*, 2154; *Angew. Chem. Int. Ed.* **1998**, *37*, 2047.
[5] a) O. Löber, M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 4366; b) M. Kawatsura, J. F. Hartwig, *Organometallics* **2001**, *20*, 1960; c) M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 9546; d) A. L. Seligson, W. C. Trogler, *Organometallics* **1993**, *12*, 744.
[6] a) M. Beller, O. R. Thiel, H. Trauthwein, C. G. Hartung, *Chem. Eur. J.* **2000**, *6*, 2513; b) S. Burling, L. D. Field, B. A. Messerle, *Organometallics* **2000**, *19*, 87; c) H. Trauthwein, A. Tillack, M. Beller, *Chem. Commun*. **1999**, 2029; d) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675; e) R. Dorta, P. Egli, F. Zürcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857; f) J.-J. Brunet, *Gazz. Chim. Ital.* **1997**, *127*, 111, and references therein; g) A. L. Casalnuovo, J. C. Calabrese, D. Milstein, *J. Am. Chem. Soc.* **1988**, *110*, 6738.
[7] a) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, J. Herwig, T. E. Müller, O. R. Thiel, *Chem. Eur. J.* **1999**, *5*, 1306; b) M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T. E. Müller, A. Zapf, *J. Organomet. Chem.* **1998**, *566*, 277; c) M. Beller, M. Eichberger, H. Trauthwein, *Angew. Chem.* **1997**, *109*, 2306; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2225.
[8] H. M. Senn, P. E. Blöchl, A. Togni, *J. Am. Chem. Soc.* **2000**, *122*, 4098.
[9] R. Kempe, *Angew. Chem.* **2000**, *112*, 478; *Angew. Chem. Int. Ed*. **2000**, *39*, 469.
[10] a) M. V. Jiménez, E. Sola, M. A. Egea, A. Huet, A. C. Francisco, F. J. Lahoz, L. A. Oro, *Inorg. Chem.* **2000**, *39*, 4868; b) H. Matsuzaka, T. Kamura, K. Ariga, Y. Watanabe, T. Okubo, T. Ishii, M. Yamashita, M. Kondo, S. Kitagawa, *Organometallics* **2000**, *19*, 216; c) M. V. Jiménez, E. Sola, A. P. Martínez, F. J. Lahoz, L. A. Oro, *Organometallics* **1999**, *18*, 1125; d) M. V. Jiménez, E. Sola, J. A. López, F. J. Lahoz, L. A. Oro, *Chem. Eur. J.* **1998**, *4*, 1398; e) L. A. Oro, M. J. Fernández, J. Modrego, J. M. López, *J. Organomet. Chem.* **1985**, *287*, 409; f) L. A. Oro, M. J. Fernández, J. Modrego, C. Foces-Foces, F. H. Cano, *Angew. Chem.* **1984**, *96*, 897; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 913.
[11] a) L. Dahlenburg, K. Herbst, *J. Chem. Soc. Dalton Trans.* **1999**, 3935; b) R. Fandos, M. Martínez-Ripoll, A. Otero, M. J. Ruiz, A. Rodríguez, P. Terreros, *Organometallics* **1998**, *17*, 1465; c) K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1201; d) M. D. Fryzuk, X. Gao, K. Joshi, P. A. MacNeil, R. L. Massey, *J. Am. Chem. Soc.* **1993**, *115*, 10581, and references therein; e) M. K. Cooper, G. J. Organ, P. A. Duckworth, K. Henrick, M. McPartlin, *J. Chem. Soc. Dalton Trans.* **1988**, 2287; f) B. Cetinkaya, M. F. Lappert, S. Toroni, *J. Chem. Soc. Chem. Commun.* **1979**, 843.
[12] a) J.-J. Brunet, G. Commenges, D. Neibecker, L. Rosenberg, *J. Organomet. Chem.* **1996**, *522*, 117; b) M. Rahim, C. H. Bushweller, K. J. Ahmed, *Organometallics* **1994**, *13*, 4952; c) M. Rahim, K. J. Ahmed, *Organometallics* **1994**, *13*, 1751; d) D. S. Glueck, L. J. N. Winslow, R. G. Bergman, *Organometallics* **1991**, *10*, 1462; e) D. S. Glueck, R. G. Bergman, *Organometallics* **1991**, *10*, 1479.
[13] a) R. Dorta, A. Togni, *Helv. Chim. Acta* **2000**, *83*, 119; b) M. K. Kolel-Veetil, A. L. Rheingold, K. J. Ahmed, *Organometallics* **1993**, *12*, 3439.
[14] a) J.-J. Brunet, J.-C. Daran, D. Neibecker, L. Rosenberg, *J. Organomet. Chem.* **1997**, *538*, 251; b) M. K. Kolel-Veetil, M. Rahim, A. J. Edwards, A. L. Rheingold, K. J. Ahmed, *Inorg. Chem.* **1992**, *31*, 3877.
[15] a) S. Kannan, A. J. James, P. R. Sharp, *Polyhedron* **2000**, *19*, 155; b) J. Ruiz, V. Rodriguez, G. López, J. Casabó, E. Molins, C. Miravitlles, *Organometallics* **1999**, *18*, 1177; c) J. J. Li, W. Li, A. J. James, T. Holbert, T. P. Sharp, P. R. Sharp, *Inorg. Chem.* **1999**, *38*, 1563; d) M. S. Driver, J. F. Hartwig, *Organometallics* **1997**, *16*, 5706; e) F. Ragaini, S. Cenini, F. Demartin, *J. Chem. Soc. Dalton Trans.* **1997**, 2855; f) L. A. Villanueva, K. A. Abboud, J. M. Boncella, *Organometallics* **1994**, *13*, 3921; g) J. Ruiz, M. T. Martinez, C. Vicente, G. García, G. López, P. A. Chaloner, P. B. Hitchcock, *Organometallics* **1993**, *12*, 4321; h) M. Kita, M. Nonoyama, *Polyhedron* **1993**, *12*, 1027; i) S. Okeya, H. Yoshimatsu, Y. Nakamura, S. Kawaguchi, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 483.
[16] a) J. F. Hartwig *Acc. Chem. Res.* **1998**, *31*, 852; b) M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1997**, *119*, 8232; c) M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc.* **1995**, *117*, 4708; d) L. A. Villanueva, K. A. Abboud, J. M. Boncella, *Organometallics* **1992**, *11*, 2963.
[17] G. Aullón, A. Lledós, S. Alvarez, *Inorg. Chem.* **2000**, *39*, 906.
[18] C. Tejel, M. A. Ciriano, M. Bordonaba, J. A. López, F. H. Lahoz, L. A. Oro, *Inorg. Chem.* **2002**, *41*, 2348.
[19] G. C. Martín, G. J. Palenik, J. M. Boncella, *Inorg. Chem.* **1990**, *29*, 2027.
[20] C. Tejel, J. M. Villoro, M. A. Ciriano, J. A. López, E. Eguizábal, F. H. Lahoz, V. I. Bakhmutov, L. A. Oro, *Organometallics* **1996**, *15*, 2967.
[21] See, for example: a) K. N. Jayaprakash, D. Conner, T. B. Gunnoe, *Organometallics* **2001**, *20*, 5254; b) K. N. Jayaprakash, T. B. Gunnoe, P. D. Boyle, *Inorg. Chem.* **2001**, *40*, 6481; c) P. L. Holland, R. A. Andersen, R. G. Bergman, *Comments Inorg. Chem.* **1999**, *21*, 115; d) P. L. Holland, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1996**, *118*, 1092; e) K. G. Caulton, *New J. Chem.* **1994**, *18*, 25; f) H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 1444.
[22] a) G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1979**, *19*, 218; b) J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.* **1974**, *15*, 18.
[23] SADABS: Area-Detector Absorption Correction; Bruker Industrial Automation, Inc., Madison, WI, **1996**.
[24] Programs for crystal structure analysis (Release 97–2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Göttingen (Germany), **1998**.

Received: February 5, 2002 [F3853]

  0947-6539/02/0814-3138 $ 17.50+.50/0