Early and Late Transition Metal Complexes Stabilised by Imidazopyridazine-Substituted Bisamido Ligands

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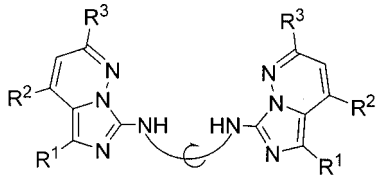
The preparation of a series of new imidazo[1,5-*b*]pyridazine-substituted diamines (**5**) is reported. They can be synthesised by the nucleophilic ring transformation of 2-amino-5-methyl-1,3,4-oxadiazolium halogenides (**1**) with diaminoalkanes followed by condensation reactions with 1,3-diketones. After deprotonation they were then used as bisamido ligands. These ligands stabilise early and late transition metal complexes as five-membered chelates. The reaction with selected group 4 metals (titanium and zirconium) leads via amine elimination to unusual dark blue and purple mononuclear amido complexes. Deprotonation of the bisamido ligands using BuLi and further reaction with group 6 metals like chromium results in a dinuclear octahedral Cr^{III} complex, where the different coordinated metal centres are bridged by two of the amido N atoms. The double deprotonation of **5** followed by reaction with the group 9 metals rhodium and iridium led to dinuclear complexes in a *trans* binding mode. The X-ray structures of one of the novel bisamido ligands (protonated) and all complexes are reported and discussed.

Introduction

Amido metal chemistry[1] has attracted much attention recently.[2] The amido ligands used to accomplish this chemistry are obtained mainly from the smooth and selective formation of Si–N bonds via salt elimination or from palladium catalysed aryl amination, which is highly efficient for forming C–N bonds.[3] Both systems have certain limitations e.g. the instability of the Si–N bond and the catalyst cost of the amination reactions. Thus we became interested in an amine synthesis protocol, which allows the synthesis of stable amido ligand precursors and the introduction of a large variety of substitution patterns. A further advantage is the classical bench top chemistry used to carry out the amine syntheses. In this paper synthesis of imidazo[1,5-*b*]-pyridazine-substituted diamines (Scheme 1) and the application of these amines as amido ligands to stabilise early and late transition metals, is reported.



Scheme 1. Imidazo[1,5-*b*]pyridazine-substituted diamines ($R^{1–3}$ aryl or alkyl substituents).

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Results and Discussion

Synthesis of the Ligand Precursors – Synthesis of the Diamines

2-Amino-5-methyl-1,3,4-oxadiazolium halogenides[4] **1** (Scheme 2) react with a large variety of primary and secondary amines to afford 2-amino-substituted 1-acetylamino-imidazoles via ring transformation.[5] Thus, the reaction with diaminoalkanes should give rise to *N*,*N*′-bis(1-acetylamino-4-alkyl/aryl-imidazol-2-yl)-1,ω-diaminoalkanes **2a**–**c** (Scheme 2).

In the course of the ring transformation one equiv. of the amine acts as a nucleophile, attacking the amine-substituted carbon atom of the oxadiazolium halide with HBr being eliminated. An excess of the amines is used to trap the HBr. Furthermore, water is eliminated and a new bond between the exocyclic N atom and the exocyclic C atom of the carbonyl group is formed. These ring transformations are extremely exothermic. Variation of the diamines and the oxadiazolium halogenides (substituent R^1) allows the formation of, for instance, **2a**–**c** (Scheme 2). Reaction of **2** with HCl in ethanol produces **3a**–**d** (deacetylation) and neutralisation with aqueous NaOH leads to **4a**–**c**.

The reactions of 1-amino-4-arylimidazoles[6] with diketones afford imidazo[1,5-*b*]pyridazines,[7] a class of substances with a very interesting potential as a suitable non-nucleoside inhibitor of HIV-1 (RT).[8] Analogously, **4** reacts

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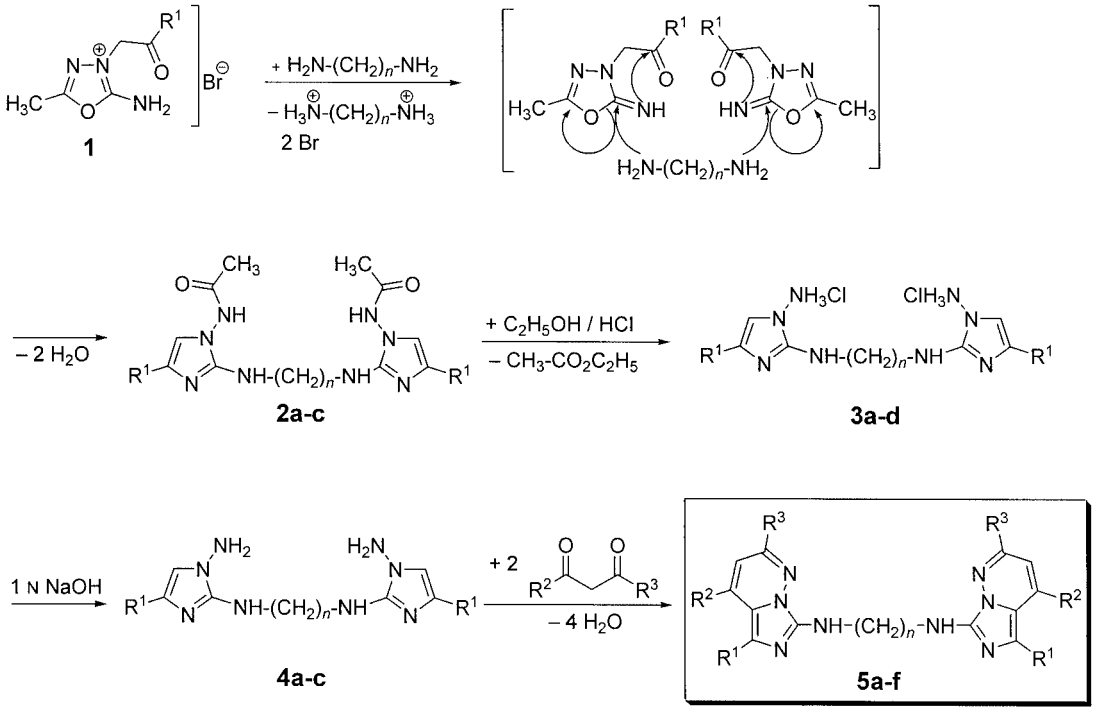


Scheme 2. Ring transformation with diaminoalkanes [n = 2: R^1 = –$C(CH_3)_3$ (**2a/3a/4a**), R^1 = C_6H_5 (**2b/3b/4b**); n = 3: R^1 = C_6H_5 (**2c/3c/4c**), R^1 = C_6H_4-$p$$CH_3$ (**3d**)] and synthesis of **5a**–**f** [n = 2: $R^1/R^2/R^3$ = –$C(CH_3)_3/CH_3/CH_3$ (**5a**), $R^1/R^2/R^3$ = -$C(CH_3)_3/C_6H_5/CH_3$ (**5b**), $R^1/R^2/R^3$ = $C_6H_5/CH_3/CH_3$ (**5c**); n = 3: $R^1/R^2/R^3$ = $C_6H_5/CH_3/CH_3$ (**5d**), $R^1/R^2/R^3$ = $C_6H_5/C_6H_5/CH_3$ (**5e**), $R^1/R^2/R^3$ = C_6H_4-$p$$CH_3/CH_3/CH_3$ (**5f**)].

with acetylacetone and/or benzoylacetone and diaminoalkyl-bridged imidazo[1,5-*b*]pyridazines **5a**–**f** (Scheme 2) are formed. The reactions with benzoylacetone lead to 2-methyl-4-phenyl-imidazopyridazines selectively, which means the methyl group is found in the 2- and the phenyl group in the 4-position. The reason for this might be the higher reactivity of the acetyl group towards the amine function of **4**. A methyl group in the 4-position is characterised by a doublet (^{1}H NMR signal) as well as the H atom in the 3-position. The splitting is about 3 Hz (both signals) and is caused by ^4J coupling due to the short C–C distances of the C–C double bond of the six-membered ring.

Substituents in the 2-(R^3), 4-(R^2) and 5-(R^1)-positions are easily modified with the synthetic protocol described above. Thus, the electronic properties, the steric demand and the solubility behaviour of the corresponding amido ligands can easily be fine-tuned. Compounds **5a**–**f** are obtained as orange to red crystalline materials in good yields after recrystallisation from ethanol water mixtures. X-ray crystal structure analysis was performed to determine the molecular structure (Figure 1) of **5a**. Experimental details are summarised in Table 1. The significantly shorter N1–C2 (1.30 Å) and C3–C4 (1.35 Å) bonds indicate the localisation of the double bonds of the six-membered pyridazine rings in **5a**. The ^{1}H NMR spectroscopic data of **5a**–**f** confirms this observation. The dihedral angles between the two-imidazopyridazine planes are 93.5° in **5a**. The deviations from planes are 0.0078 Å and 0.0071 Å. Both 7-substituted amido N atoms are in the plane with the imidazopyridazines. The deviations of the N1 and N5 atoms, out of the imidazopyridazine planes, are 0.0135 Å and 0.0097 Å, respectively. Complex **5a** is predicted to form inter- or intramolecular H bonds because it contains potential proton donor and acceptor functionalities. An intramolecular hydrogen bond[9] N5–HN5···N2 (with a HN5···N2 distance of 2.40 Å) forces **5a** into a transoid arrangement.

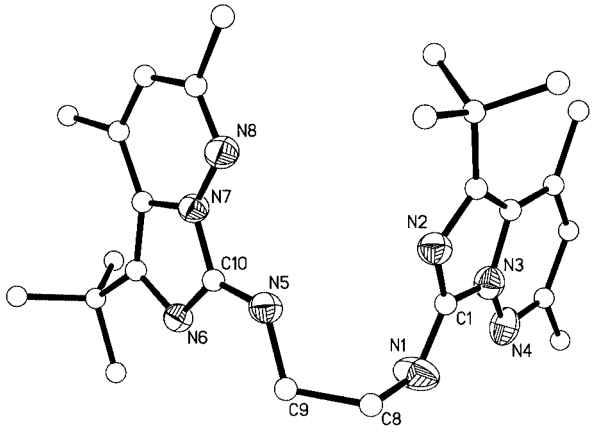


Figure 1. Molecular structure of **5a**; selected bond lengths [Å] and angles [°]: C1–N1 1.360(3), C1–N3 1.343(2), C1–N2 1.313(2), C8–N1 1.441(2), C9–N5 1.451(2), C10–N6 1.319(2), C10–N5 1.368(2), C10–N7 1.346(2), N3–N4 1.369(2), N7–N8 1.369(2), C8–C9 1.509(3); N1–C1–N3 120.95(17), N1–C1–N2 127.37(17), N3–C1–N2 111.68(16), C1–N3–N4 122.50(16), N5–C10–N7 122.06(15), N5–C10–N6 126.82(15), N7–C10–N6 111.11(14).

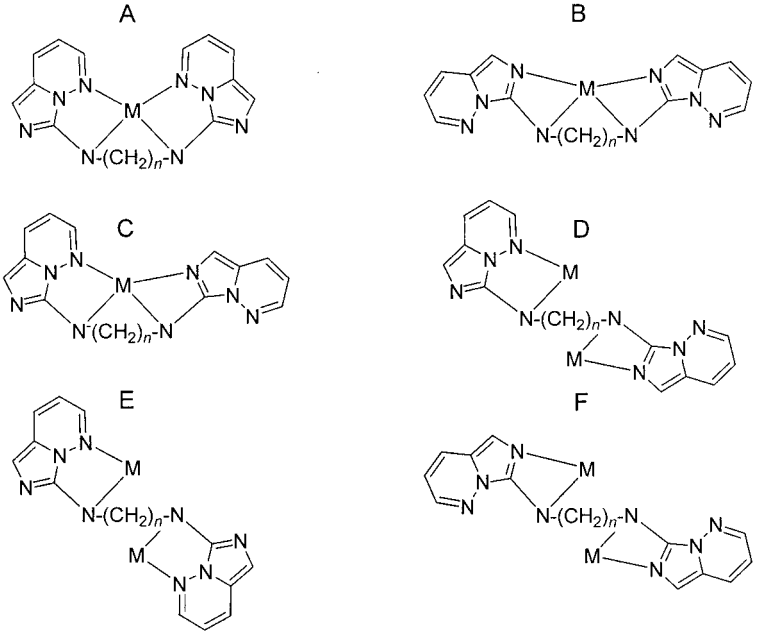
Table 1. Details of the X-ray crystal structure analyses of **5a**, **6** and **7**.

	5a	**6**	**7**
Formula	$C_{26}H_{38}N_8$	$C_{26}H_{36}Cl_2N_8Ti$	$C_{34}H_{56}N_{10}Zr$
M [g mol^{-1}]	462.62	579.38	696.08
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*21/*c*	*P*21/*n*	*P*2/*c*
a [Å]	9.5144(4)	10.347(1)	11.740(1)
b [Å]	12.8021(8)	9.506(1)	9.315(1)
c [Å]	21.3187(9)	30.407(3)	17.418(2)
β [°]	97.306(3)	97.65(1)	109.16(1)
V [Å^3]	2575.6(2)	2964(1)	1799(1)
Z	4	4	4
Crystal size [mm]	0.60 × 0.50 × 0.40	0.38 × 0.08 × 0.03	0.30 × 0.30 × 0.20
$\rho_{calcd.}$ [g cm^{-3}]	1.193	1.298	1.285
$\mu_{calcd.}$ [mm^{-1}] (Mo-K_α)	0.074	0.499	0.344
T [K]	193(2)	193(2)	200(2)
θ range [°]	1.86–25.71	2.18–25.83	1.84–24.26
Reflections collected	4865	5445	2862
Independent reflections	3834	2727	2240
F(000)	1000	1216	740
R value [$I > 2\sigma(I)$]	0.0497	0.0521	0.0474
wR_2 (all data)	0.1456	0.1238	0.1240

Complex Syntheses and Structures

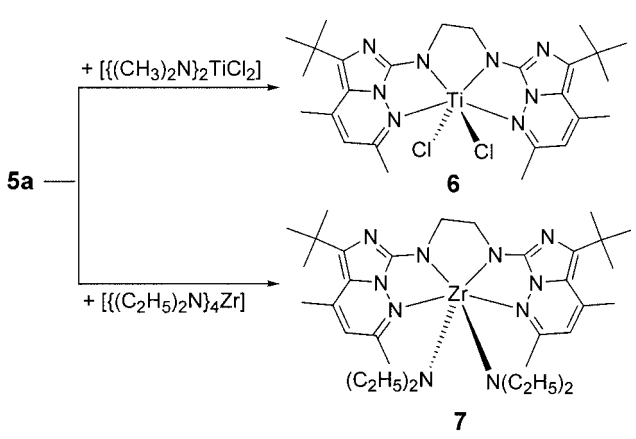
Compounds **5** as well as the deprotonated versions have six different donor functions to coordinate transition metals. Thus, a range of binding modes depending on the nature of the transition metal as well its oxidation state, are expected. Possible binding modes of double deprotonated **5** are shown in Scheme 3.

A cisoid/transoid orientation concerning the diamido unit can be considered as well as the formation of four- or five-membered chelates. Thus, the binding modes A (*cis*55), B (*cis*44), C (*cis*45), D (*trans*45), E (*trans*55) and F (*trans*44) are expected (*cis* = cisoid, *trans* = transoid, 4 = four-membered and 5 = five-membered chelates). Coordination chemical studies were performed with **5a**. Group 4 metal complexes are efficiently accessible via amine elimination reactions,[2,10] especially since the availability of a variety of amido and mixed amido chloro starting material complexes.[11] The reaction of **5a** with one equiv. of bis(dimethylamido)titanium dichloride gave rise to **6** as a dark blue-purple crystalline material (Scheme 4). Due to the good solubility of **5a** in nonpolar solvents the reaction was accomplished in ether. We wondered about the dark blue to purple colour since titanium amides are usually red coloured and thus put the colour change down to the deprotonation of the ligand. The reaction of **5a** with tetrakis(di-



Scheme 3. Binding modes A (*cis*55), B (*cis*44), C (*cis*54), D (*trans*45), E (*trans*55) and F (*trans*44) of double deprotonated **5**.

ethylamido)zirconium, during which **7** is formed as a crystalline purple material in high yield (Scheme 4) goes along with such a colour change, and supports this hypothesis since zirconium amides are usually colourless. The UV/Vis spectra of **5a**, **6** and **7** are shown in Figure 2. The optical spectra were recorded in C_6H_6 using the same concentrations for all compounds. The ligand shows a significant lower absorption (abs < 0.2) over a plateau with a major peak at 511.0 nm. The longer UV absorption wavelengths of the complexes **6** (626.0 nm) and **7** (572.3 nm, 553.9 nm) were consistent with the observed colour of **6** and **7** in the solid states and in solutions with different solvents. These absorption wavelengths indicate transitions between d levels of the metal ions. The shorter UV absorption wavelengths of **6** (422.0 nm) and **7** (520.0 nm, 347.6 nm) are attributed to electron transitions between the metal ion and ligand or within the ligand.[12] The NMR spectra of **6** and **7** show a single signal set of deprotonated **5a** and thus were indicative of the formation of mononuclear complexes.



Scheme 4. Synthesis of **6** and **7** via amine elimination.

An X-ray crystal structure analysis of **6** and **7** was performed. Experimental details are summarised in Table 1. The molecular structures of **6** and **7** are shown in Figure 3 and Figure 4, respectively. Both compounds are best described as octahedrally coordinated and adopt the *cis*55 binding mode. The $M–N_{pyridazine}$ bond lengths in **6** (2.313 Å, 2.307 Å) and **7** (2.562 Å) are significantly longer than the $M–N_{amido}$ bond lengths (**6** = 1.973 Å, 1.991 Å; **7** = 2.184 Å), which indicates localised bonding modes for the five-membered chelates of both complexes . The $N_{amido}–Ti–N_{pyridazine}$ angle of the five-membered chelate (mean = 74.8°) is 6.3° larger and the $N_{amido}–Ti–N_{amido}$ (75.57°) is 4.8° larger than the corresponding angle in **7**. The Cl–Ti–Cl angle of the two chloro ligands and the N–Zr–N angles of the two diethylamido ligands are 138° and 123°, respectively. Considering the ideal angles in an octahedral scenario, 90° or 180° for these additional ligands, the smaller titanium seems closer to a *trans* arrangement and the larger zirconium closer to a *cis* arrangement. The dihedral angles

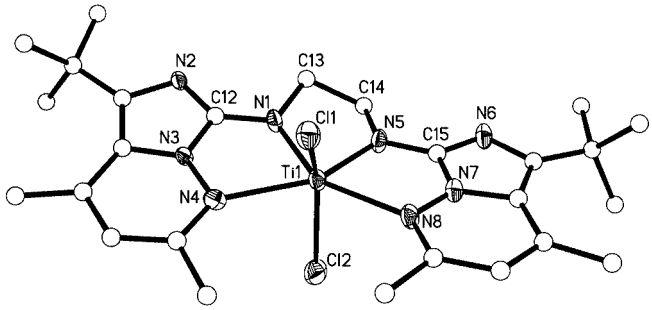


Figure 3. Molecular structure of **6**; selected bond lengths [Å] and angles [°]: Ti1–N1 1.973(4), Ti1–N5 1.991(4), Ti1–N4 2.313(4), Ti1–N8 2.307(4), Ti1–Cl1 2.328(15), Ti1–Cl2 2.329(14); N1–Ti1–N5 75.57(15), N1–Ti1–N8 149.34(14), N5–Ti1–N8 74.78(14), N1–Ti1–N4 74.85(14), N5–Ti1–N4 149.14(14), Cl1–Ti1–Cl2 138.37(6), N7–C15–N5 116.7(4), N7–N8–Ti1 107.8(2), C15–N5–Ti1 120.7(3).

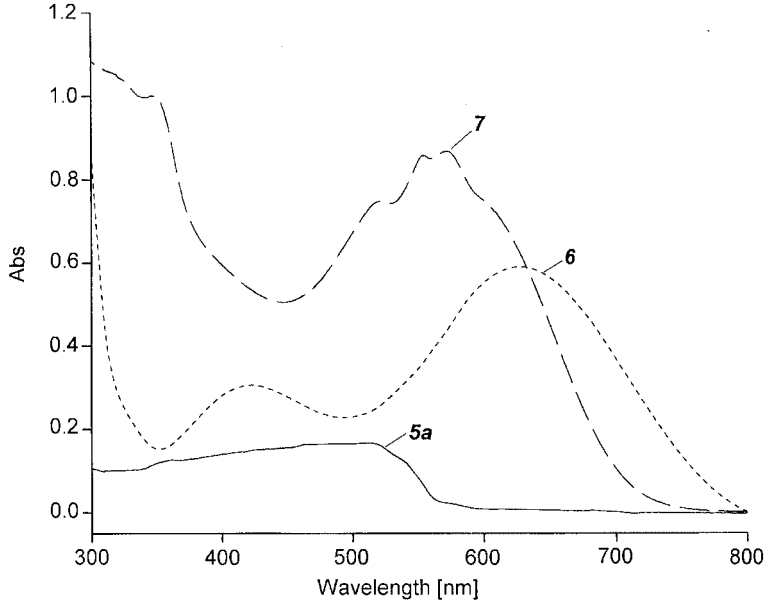


Figure 2. UV/Vis spectra of **5a**, **6** and **7** in C_6H_6.

between the two imidazopyridazine planes are 15° in **6** and 27.2° in **7**. The deviations from planes are 0.0115 Å and 0.0140 Å in **6** and 0.035 Å for both imidazopyridazines in **7**.

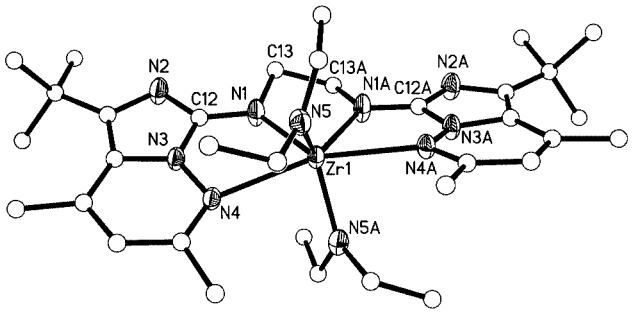
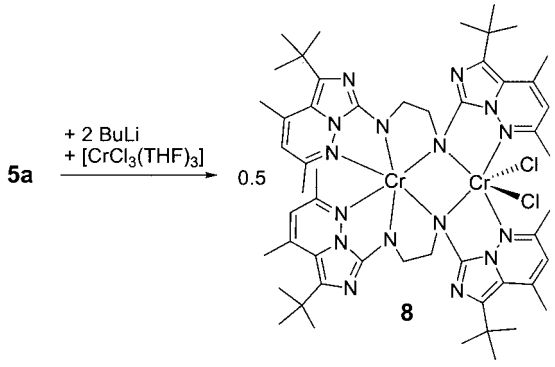


Figure 4. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: Zr1–N1 2.184(3), Zr1–N5 2.007(3), Zr1–N4 2.562(3); N1–Zr1–N5 104.98(13), N1–Zr1–N4 68.54(10), N1–Zr1–N1A 70.77(16), N4–Zr1–N5 83.82(11), N5–Zr1–N5A 123.88(17), C12–N3–N4 120.4(3), N1–C12–N3 118.4(3), C13–N1–Zr1 121.4(2).

Group 6 metal amides do not eliminate as efficiently as group 4 metals and the variety of possible starting materials is much smaller. Thus the opportunities of salt metathesis reactions to synthesise chromium complexes were explored. The double lithiation of **5a** at –70 °C and the reaction of this mixture with $[CrCl_3(THF)_3]$ (THF = tetrahydrofuran) led to the crystalline material of the paramagnetic chromium complex **8** (Scheme 5). Due to the paramagnetic nature of this compound, structural characterisation by NMR spectroscopic methods was not of much help.

The molecular structure was explored by X-ray analysis. Experimental details are summarised in Table 2. The molecular structure of **8** is shown in Figure 5, and includes selected bond lengths and angles. Compound **8** is a dinuclear dichloro chromium(III) complex. Both chromium atoms adopt an octahedral coordination, as preferred by Cr^{III}



Scheme 5. Synthesis of **8**.

complexes,[13] bridged by two of the amido N atoms (Scheme 6). Cr^{III}, d^3, is the most stable and important state and octahedral complexes must have three unpaired electrons irrespective of the strength of the ligand field, giving a sort of half-filled shell stability. The magnetic moment of **8** is μ_{eff} = 4.28 μ_B. The chromium–chromium distance of 3.110 Å does not indicate a direct metal–metal interaction.

The Cl–Cr–Cl angle is 94° and fits well the octahedral coordination. Both chloro ligands are in the plane with the almost square-planar four-membered ring of Cr2, N13, Cr1 and N4 (deviation from plane 0.0072 Å) (Scheme 6). The bond lengths observed between N13–Cr1(Cr2) and N4–Cr1(Cr2) reflect a delocalised bonding mode. The lengths of the $Cr–N_{pyridazine}$ bonds are almost 0.20 Å longer than the $Cr–N_{amido}$ bonds. This difference indicates a localised bonding mode. The flexible coordination mode of the bis(imidazopyridazine) ligands allows a coordinative saturation of the metal centres, leaving two amido N atoms for bridging of two chromium(III) atoms.

Group 9 metal amides such as the late metal amido complexes are rarely described in general.[14] The mismatch of

Table 2. Details of the X-ray crystal structure analyses of **8**, **9** and **10**.

	8	**9**	**10**
Formula	$C_{52}H_{72}Cl_2Cr_2N_{16}$	$C_{42}H_{60}Ir_2N_8$	$C_{42}H_{60}N_8Rh_2$
M [g mol^{-1}]	1096.10	1061.38	882.78
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P21/a$
a [Å]	16.211(2)	13.359(3)	10.002(1)
b [Å]	18.948(2)	13.660(3)	25.587(2)
c [Å]	21.293(2)	19.280(4)	10.810(1)
α [°]	95.010(10)	92.26(3)	
β [°]	104.150(10)	104.63(3)	115.390(1)
γ [°]	94.010(10)	114.48(3)	
V [Å^3]	6289.5(12)	3056.7(11)	2499.3(18)
Z	4	3	4
Crystal size [mm]	0.30 × 0.30 × 0.10	0.24 × 0.18 × 0.16	0.40 × 0.26 × 0.21
$\rho_{calcd.}$ [g cm^{-3}]	1.265	1.730	1.418
$\mu_{calcd.}$ [mm^{-1}] (Mo-K_α)	0.483	6.564	0.706
T [K]	293(2)	293(2)	193(2)
θ range [°]	1.30–21.09	1.78–26.06	2.23–25.85
Reflections collected	12665	20282	4513
Independent reflections	4492	10906	3908
F(000)	2543	1566	1116
R value [$I > 2\sigma(I)$]	0.0772	0.0460	0.0283
wR_2 (all data)	0.2073	0.1282	0.0812

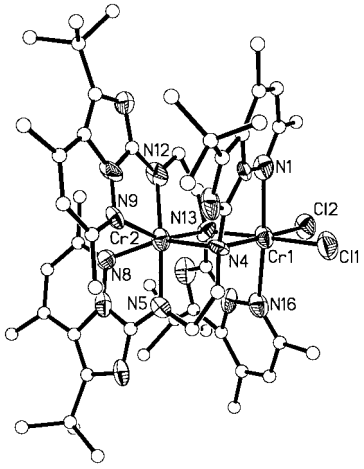
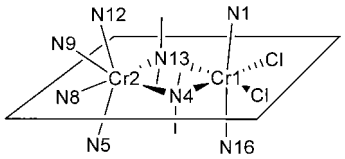
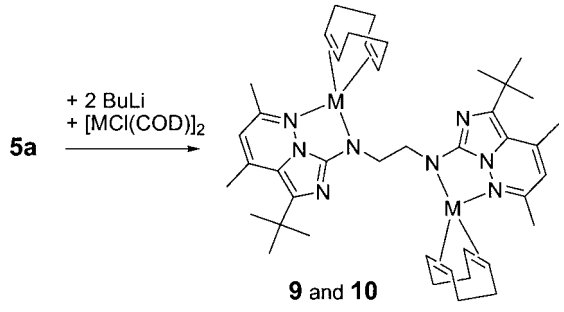


Figure 5. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: N4–Cr1 2.088(8), N4–Cr2 2.065(10), N13–Cr1 2.082(10), N13–Cr2 2.071(8), Cr1–Cl1 2.309(4), Cr1–Cl2 2.319(3), N1–Cr1 2.212(10), N16–Cr1 2.218(11), N12–Cr2 1.987(10), N5–Cr2 2.023(10), N9–Cr2 2.224(9), N8–Cr2 2.198(11); N4–Cr2–N13 84.6(4), N4–Cr1–N13 83.7(3), Cr1–N13/N4–Cr2 95.8(4), Cl1–Cr1–Cl2 93.88(13), N1–Cr1–N16 175.2(3), N12–Cr2–N5 176.5(4), N8–Cr2–N9 94.5(3), N9–Cr2–N12 78.4(4), N8–Cr2–N5 77.8(4).



Scheme 6. Coordination sphere of **8**.

the rather hard amido ligands and the soft nature of the late transition metals might be one of the reasons for this shortage.[15] The most studied amido compounds of iridium and rhodium are dinuclear complexes containing the chelating and bridging ligands[16] and mononuclear complexes with chelating bifunctional ligands.[17] Dinuclear amido iridium[18] and rhodium[19] complexes with simple amides ($RR'N^-$ and RHN^-), as well as the very reactive mononuclear compounds[20] with these amides, have been scarcely studied. The double deprotonation of **5a** (using BuLi) followed by the reaction with $[IrCl(COD)]_2$ or $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) led to the group 9 metal amides **9** and **10** (Scheme 7). The ^1H and ^{13}C NMR spectroscopic data of **9** and **10** are similar, taking into consideration the fact that characteristic ligand signals are slightly



Scheme 7. Synthesis of **9** (M = Ir) and **10** (M = Rh).

different. Thus, only the spectra of **9** are discussed. Its ^1H NMR spectra exhibit a single signal and a doublet for the methyl groups and single signals at 1.5 ppm for the *tert*-butyl group and 3.8 ppm for the bridging CH_2. Furthermore, the H atom in the 3-position is characterised by a doublet as well as the methyl group in the 4-position. The splitting is about 1 Hz (both signals) and is caused by ^4J coupling. The coordinated COD ligand on the metal centre gives two broad signals for the CH and two broad multiplies for the CH_2 group. Thus, **9** and **10** possess symmetry

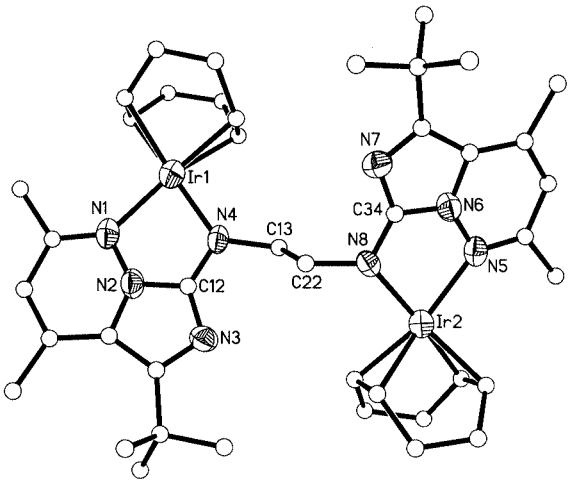


Figure 6. Molecular structure of **9**; selected bond lengths [Å] and angles [°]: Ir1–N4 2.005(7), Ir1–N1 2.141(7), Ir2–N8 2.033(7), Ir2–N5 2.166(7), N1–N2 1.390(10), N2–C12 1.340(10), N3–C12 1.345(11), N4–C12 1.357(11), N4–C13 1.475(10), C13–C22 1.542(12), N8–C22 1.474(10), N8–C34 1.343(11), N7–C34 1.354(12), N6–C34 1.339(10), N5–N6 1.388(10); N1–Ir1–N4 80.3(3), C12–N2–N1 119.6(7), C12–N4–C13 114.4(7), C12–N4–Ir1 113.9(5), N2–N1–Ir1 107.7(5), N8–Ir2–N5 79.3(3), C34–N8–Ir2 113.5(5), N6–N5–Ir2 107.1(4), C34–N6–N5 120.0(7), C34–N8–C22 114.9(7).

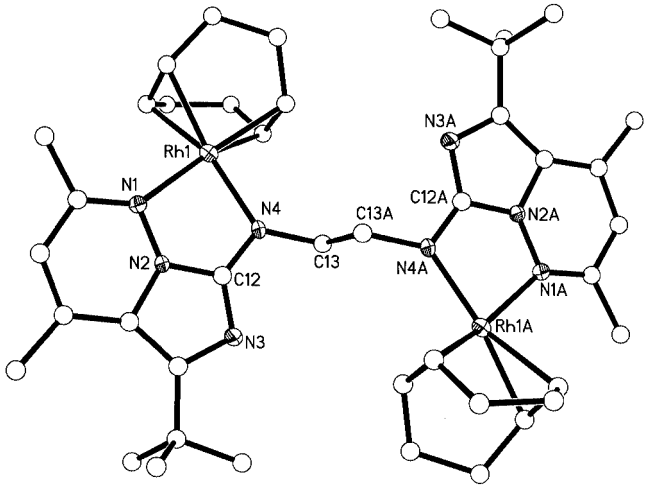


Figure 7. Molecular structure of **10**; selected bond lengths [Å] and angles [°]: Rh1–N4 2.055(2), Rh1–N1 2.164(2), N1–N2 1.389(3), N2–C12 1.345(4), N3–C12 1.348(3), N4–C12 1.348(3), N4–C13 1.456(3), C13–C13A 1.531(5); N1–Rh1–N4 80.41(8), C12–N2–N1 121.3(2), C12–N4–C13 116.0(2), C12–N4–Rh1 111.41(17), N2–N1–Rh1 105.43(15).

in solution and only signals for half of the complexes are observed. The molecular structures (solid state) of **9** and **10** are shown in Figure 6 and Figure 7, respectively. Experimental details are summarised in Table 2.

In **9** and **10** deprotonated **5a** binds two metal centres accomplishing the *trans*55 binding mode. These dinuclear complexes are better described as mononuclear complexes with chelating bifunctional ligands in which only the ligands over an alkyl bridge are connected. Compounds **9** and **10** are not isostructural in the solid state.

Conclusions

The results of the present work allow several conclusions to be drawn. The alkyl-bridged imidazopyridazine-substituted bisamines can be synthesised by nucleophilic ring transformation followed by condensation reactions from nonexpensive starting materials in good yields, in large variety and in high purity. The deprotonated diamines can act as bisamido ligands. These ligands bind early and late transition metals as a five-membered chelate. Group 4 metal complexes are accessible via amine elimination and group 6 and 9 metal complexes via salt elimination reactions. In summary, we introduced a novel amido ligand system.

Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and glove box techniques. Non-halogenated solvents were distilled from sodium benzophenone ketyl and halogenated solvents from P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. $[Ti(NMe_2)_2Cl_2]$ was prepared according a literature method.[11] All chemicals were purchased from commercial vendors and used without further purification. NMR spectra were obtained using either a Bruker ARX 250 or Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analyses were performed by using a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[21] SHELXL-97[22] and WinGX.[23] Crystallographic details are summarised in Table 1 and Table 2. CCDC-267047 (for **5a**), -267042 (for **6**), -267044 (for **7**), -267043 (for **8**), -267046 (for **9**) and -267045 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Elemental analyses were carried out by the Vario elementar EL *III* or Leco CHNS-932 elemental analyser. Melting points were carried out in sealed capillaries, with a Büchi 535 apparatus or Stuart SMP3 apparatus. UV spectroscopic studies were carried out with a Varian CARY 3. The magnetic moment was determined with a magnetic susceptibility balance Sherwood Mark 1 MSB at room temperature.

Synthesis of Ligands and Ligand Precursors

***N*,*N*′-Bis(1-acetylamino-4-*tert*-butylimidazol-2-yl)ethylenediamine Hydrate (2a):** Ethylenediamine (0.48 mL, 0.43 g, 7.19 mmol) was added to 2-amino-5-methyl-3-(2-oxo-3,3-dimethylbutyl)-1,3,4-oxadiazolium bromide (2.00 g, 7.19 mmol) whilst stirring. The mixture was stirred for 1 min on a hot plate (250 °C) and was then allowed to reach room temperature. Water (20 mL) was added to the reaction mixture and colourless crystals formed after some hours. The product was recrystallised from ethanol/water (1:1 ratio). Yield 0.74 g (44%), m.p.146 °C. $C_{20}H_{34}N_8O_2{\cdot}2.5H_2O$ (463.53): calcd. C 51.82, H 8.84, N 24.17; found C 51.96, H 7.84, N 24.46. ^{1}H NMR ([D$_6$]DMSO): δ = 10.73 (sbs, 1 H, NH, acetylamino), 6.46 (s, 1 H, H-5, imidazole), 6.19 (br. s, 1 H, *NH*–CH_2), 3.57 (s, 2 H, CH_2), 2.18 (s, 3 H, CH_3), 1.38 [s, 9 H, –C*(CH$_3$)$_3$*] ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 169.21 (C=O), 148.35 (C-2, imidazole), 143.14 (C-4, imidazole), 108.67 (C-5, imidazole), 42.61 (CH_2), 31.52 [–*C*(CH_3)$_3$], 29.91 [–C*(CH$_3$)$_3$*], 21.15 (CH_3) ppm.

***N*,*N*′-Bis(1-acetylamino-4-phenylimidazol-2-yl)ethylenediamine (2b):** 2-Amino-5-methyl-3-phenacyl-1,3,4-oxadiazolium bromide (2.00 g, 6.72 mmol) and ethylenediamine (0.44 mL, 0.40 g, 6.72 mmol) were stirred for 1 min on a hot plate (250 °C) and then allowed to reach room temperature. After cooling to room temperature water was added. The resulting solid was recrystallised from ethanol. Yield 0.65 g (42%), m.p. 160 °C. $C_{24}H_{26}N_8O_2$ (458.48). ^{1}H NMR ([D$_6$]-DMSO): δ = 10.71 (s, 1 H, NH, acetylamino); 7.69–7.67 (d, 2 H, H$_o$, C_6H_5); 7.32–7.27 (t, 2 H, H$_m$, C_6H_5); 7.15–7.10 (t, 1 H, H$_p$, C_6H_5); 7.12 (s, 1 H, H-5, imidazole); 6.11 (br. s, 1 H, *NH*–CH_2); 3.49 (br. s, 2 H, *CH_2*–NH); 1.95 (s, 3 H, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 168.78 (C=O); 149.25 (C-2, imidazole); 134.81 (C-1′, C_6H_5); 133.38 (C-4, imidazole); 128.11, 123.65 (C$_{o,m}$, C_6H_5); 125.48 (C$_p$, C_6H_5); 111.93 (C-5, imidazole); 42.34 (*CH_2*–NH); 20.64 (CH_3) ppm.

***N*,*N*′-Bis(1-acetylamino-4-phenylimidazol-2-yl)-1,3-diaminopropane Monohydrate (2c):** 1,3-Diaminopropane (0.56 mL, 0.50 g, 6.71 mmol) was added dropwise to 2-amino-5-methyl-3-phenacyl-1,3,4-oxadiazolium bromide (2.00 g, 6.71 mmol) and the reaction mixture was stirred for 1 min on a hot plate (250 °C). After cooling to room temperature water was added. The resulting solid was recrystallised from ethanol and a colourless product was obtained. Yield 0.57 g (34%), m.p. 179 °C. $C_{25}H_{28}N_8O_2{\cdot}H_2O$ (490.50): calcd. C 61.21, H 6.17, N 22.85; found C 61.55, H 5.85, N 22.85. ^{1}H NMR ([D$_6$]DMSO): δ = 10.98 (br. s, 1 H, NH, acetylamino), 7.93–7.92 (d, 2 H, H$_o$, C_6H_5), 7.57–7.53 (q, 2 H, H$_m$, C_6H_5), 7.40–7.38 (d, 1 H, H$_p$, C_6H_5), 7.36 (s, 1 H, H-5, imidazole), 6.32–6.29 (t, 1 H, *NH*–CH_2), 3.59–3.55 (q, 2 H, *CH_2*–NH), 2.20 (s, 3 H, CH_3), 2.15–2.09 (m, 1 H, *0,5CH_2*–CH_2–NH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 169.25 (C=O), 149.84 (C-2, imidazole), 135.29 (C-1′, C_6H_5), 133.86 (C-4, imidazole), 128.60, 124.08 (C$_{o,m}$, C_6H_5), 125.90 (C$_p$, C_6H_5), 112.27 (C-5, imidazole), 40.27 (CH_2–NH), 29.86 (*CH_2*–CH_2–NH), 21.15 (CH_3) ppm.

***N*,*N*′-Bis(1-amino-4-*tert*-butylimidazol-2-yl)ethylenediamine Dihydrochloride Dihydrate (3a):** Concentrated aqueous HCl (1.5 mL) was slowly added to a stirred suspension of *N*,*N*′-bis(1-acetylamino-4-*tert*-butylimidazol-2-yl)ethylenediamine hydrate (1.50 g, 3.24 mmol) in ethanol (20 mL). The mixture was heated for 1.5 h under reflux. The solvent was removed and colourless crystals were obtained and recrystallised from ethanol. Yield 1.40 g (98%), m.p. 230 °C. $C_{16}H_{30}N_8{\cdot}2HCl{\cdot}2H_2O$ (443.37): calcd. C 43.34, H 8.18, N 25.27; found C 42.98, H 7.81, N 25.02. ^{1}H NMR ([D$_6$]-DMSO): δ = 12.82 (s, 1 H, HCl), 8.01 (s, 1 H, NH), 6.76 (s, 1 H, H-5, imidazole), 6.15 (br. s, 2 H, NH_2), 3.89–3.88 (t, 2 H, CH_2), 1.44 [s, 9 H, –C*(CH$_3$)$_3$*] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 146.76 (C-2, imidazole), 133.62 (C-4, imidazole), 112.66 (C-5, imidazole), 42.44 (CH_2), 30.72 [–*C*(CH_3)$_3$], 29.04 [–C*(CH$_3$)$_3$*] ppm.

***N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)ethylenediamine Dihydrochloride Trihydrate (3b):** Concentrated aqueous HCl (3 mL) was slowly added to a suspension of *N*,*N*′-bis(1-acetylamino-4-phenyl-

imidazol-2-yl)ethylenediamine (1.85 g, 4.04 mmol) in ethanol (15 mL). The stirred reaction mixture was refluxed for 3 h. The solvent was removed and the resulting crystalline product was recrystallised from ethanol/water (ratio 2:1). Yield 1.62 g (80%), m.p. 262 °C. $C_{20}H_{22}N_8{\cdot}2HCl{\cdot}3H_2O$ (501.36): calcd. C 47.90, H 6.03, N 22.35; found C 47.75, H 5.62, N 22.49. ^{1}H NMR ([D$_6$]-DMSO): δ = 13.01 (br. s, 1 H, HCl), 8.16 (br. s, 1 H, NH), 7.89–7.87 (d, 2 H, H$_o$, C$_6$H$_5$), 7.55 (s, 1 H, H-5, imidazole), 7.45–7.40 (t, 2 H, H$_m$, C$_6$H$_5$), 7.36–7.31 (t, 1 H, H$_p$, C$_6$H$_5$), 6.16 (br. s, 2 H, NH$_2$), 3.87 (br. s, 2 H, *CH$_2$*–NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 147.07 (C-2, imidazole), 128.64, 124.73 (C$_{o,m}$, C$_6$H$_5$), 127.88 (C$_p$, C$_6$H$_5$), 127.54 (C-1′, C$_6$H$_5$), 123.65 (C-4, imidazole), 115.29 (C-5, imidazole), 41.96 (*CH$_2$*–NH) ppm.

***N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)-1,3-diaminopropane Dihydrochloride Hydrate (3c):** Concentrated aqueous HCl (1 mL) was added to a stirred solution of *N*,*N*′-bis(1-acetylamino-4-phenylimidazol-2-yl)-1,3-diaminopropane monohydrate (1.90 g, 3.87 mmol) in ethanol (20 mL). The reaction mixture was refluxed for 30 min. The solvent was removed and the resulting crystalline product was recrystallised from ethanol/water (ratio 1:1). Yield 0.60 g (32%), m.p. 263 °C. $C_{21}H_{24}N_8{\cdot}2HCl{\cdot}1.5H_2O$ (488.37): calcd. C 51.64, H 5.9, N 22.94; found C 51.82, H 5.85, N 22.55. ^{1}H NMR ([D$_6$]DMSO): δ = 13.04 (br. s, 1 H, HCl), 8.34–8.31 (t, 1 H, NH), 8.11–8.09 (d, 2 H, H$_o$, C$_6$H$_5$), 7.73 (s, 1 H, H-5, imidazole), 7.62–7.59 (t, 2 H, H$_m$, C$_6$H$_5$), 7.54–7.51 (t, 1 H, H$_p$, C$_6$H$_5$), 6.39 (s, 2 H, NH$_2$), 3.93–3.91 (bd, 2 H, *CH$_2$*–NH), 2.16–2.13 (br. t, 1 H, ½ CH$_2$–CH$_2$–NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 147.53 (C-2, imidazole), 128.99, 125.17 (C$_{o,m}$, C$_6$H$_5$), 128.24 (C$_p$, C$_6$H$_5$), 127.89 (C-1′, C$_6$H$_5$), 123.93 (C-4, imidazole), 115.73 (C-5, imidazole), 40.05 (CH$_2$–NH), 29.31 (*CH$_2$*–CH$_2$–NH) ppm.

***N*,*N*′-Bis[1-amino-4-(4-methylphenyl)-imidazol-2-yl]-1,3-diaminopropane Dihydrochloride (3d):** 1,3-Diaminopropane (0.54 mL, 0.48 g, 6.41 mmol) was added to 2-amino-5-methyl-3-(4-methylphenacyl)-1,3,4-oxadiazolium bromide (2.00 g, 6.41 mmol) whilst stirring. The mixture was stirred for 1 min on a hot plate (250 °C) and then allowed to reach room temperature. The resulting product was suspended in 20 mL of ethanol and 2 mL of concd. aqueous HCl was slowly added. The reaction mixture was refluxed whilst stirring for 2 h. The solvent was removed and a colourless crystalline crude product was recrystallised from ethanol. Yield 1.52 g (97%), m.p. 263 °C. $C_{23}H_{28}N_8{\cdot}2HCl$ (489.41): calcd. C 56.44, H 6.18, N 22.90; found C 56.26, H 6.18, N 22.51. ^{1}H NMR ([D$_6$]-DMSO): δ = 12.88 (br. s, 1 H, HCl), 8.22 (s, 1 H, NH), 7.94 (d, 2 H, H$_o$, C$_6$H$_4$), 7.62 (s, 1 H, H-5, imidazole), 7.39–7.37 (d, 2 H, H$_m$, C$_6$H$_4$), 6.30 (s, 2 H, NH$_2$), 3.87–3.82 (q, 2 H, *CH$_2$*–NH), 2.50 (s, 3 H, CH$_3$), 2.11–2.08 (m, 1 H, *0,5CH$_2$*–CH$_2$–NH) ppm. ^{13}CNMR ([D$_6$]DMSO): δ = 147.39 (C-2, imidazole), 137.73 (*C*–CH$_3$, C$_6$H$_4$), 129.58, 125.14 (C$_{o,m}$, C$_6$H$_4$), 121.44 (C-1′, C$_6$H$_4$), 115.10 (C-5, imidazole), 115.07 (C-4, imidazole), 40.01 (*CH$_2$*–NH), 29.27 (*CH$_2$*–CH$_2$–NH), 21.13 (CH$_3$) ppm.

***N*,*N*′-Bis(1-amino-4-*tert*-butylimidazol-2-yl)ethylenediamine Monohydrate (4a):** Aqueous NaOH (1 N) was added dropwise to a solution of *N*,*N*′-bis(1-amino-4-*tert*-butylimidazol-2-yl)ethylenediamine dihydrochloride dihydrate (1.20 g, 2.71 mmol) in water (10 mL) to attain a basic pH. The resulting colourless solid was recrystallised from ethanol. Yield 0.79 g (83%), m.p. 187 °C. $C_{16}H_{30}N_8{\cdot}H_2O$ (352.47): calcd. C 54.52, H 9.15, N 31.79; found C 54.59, H 9.10, N 31.98. ^{1}H NMR ([D$_6$]DMSO): δ = 6.30 (s, 1 H, H-5, imidazole), 5.52 (br. s, 1 H, NH), 5.37 (s, 2 H, NH$_2$), 3.45 (s, 2 H, CH$_2$), 1.24 [s, 9 H, –C(CH$_3$)$_3$] ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.13 (C-2, imidazole), 143.10 (C-4, imidazole), 109.52 (C-5, imidazole), 43.42 (CH$_2$), 31.54 [–*C*(CH$_3$)$_3$], 30.24 [–C*(CH$_3$)$_3$*] ppm.

***N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)ethylenediamine (4b):** *N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)ethylenediamine dihydrochloride (1.10 g, 2.46 mmol) was dissolved in water (10 mL). Aqueous NaOH (1 N) was added dropwise to this solution in order to obtain a basic pH and a colourless product was recovered. The product was recrystallised from ethanol. Yield 0.83 g (90%), m.p. 225 °C. $C_{20}H_{22}N_8$ (374.43): calcd. C 64.15, H 5.92, N 29.93; found C 63.98, H 5.74 N 29.48. ^{1}H NMR ([D$_6$]DMSO): δ = 7.69–7.66 (d, 2 H, H$_o$, C$_6$H$_5$), 7.29–7.23 (t, 2 H, H$_m$, C$_6$H$_5$), 7.10–7.05 (t, 1 H, H$_p$, C$_6$H$_5$), 7.09 (s, 1 H, H-5, imidazole), 5.81 (br. s, 1 H, NH), 5.50 (s, 2 H, NH$_2$), 3.52–3.50 (t, 2 H, CH$_2$) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 150.05(C-2, imidazole), 135.43 (C-1′, C$_6$H$_5$), 132.38 (C-4, imidazole), 128.14, 123.55 (C$_{o,m}$, C$_6$H$_5$), 125.07 (C$_p$, C$_6$H$_5$), 113.19 (C-5, imidazole), 43.10 (CH$_2$) ppm.

***N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)-1,3-diaminopropane Hemihydrate (4c):** *N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)-1,3-diaminopropane dihydrochloride hydrate (1.13 g, 2.31 mmol) was dissolved in 10 mL of water/ethanol (ratio 2:1). Aqueous NaOH (1 N) was added dropwise to this solution in order to obtain a basic pH. The resulting solid was recrystallised from ethanol and a beige product was obtained. Yield 0.78 g (85%), m.p. 161 °C. $C_{21}H_{24}N_8{\cdot}½H_2O$ (397.46): calcd. C 63.46, H 6.34, N 28.19; found C 63.89, H 6.15, N 28.15. ^{1}H NMR ([D$_6$]DMSO): δ = 7.83–7.82 (d, 2 H, H$_o$, C$_6$H$_5$), 7.42–7.38 (t, 2 H, H$_m$, C$_6$H$_5$), 7.23–7.19 (m, 1 H, H$_p$, C$_6$H$_5$), 7.22 (s, 1 H, H-5, imidazole), 5.88–5.85 (t, 1 H, NH), 5.68 (s, 2 H, NH$_2$), 3.52–3.48 (q, 2 H, *CH$_2$*–NH), 2.00–1.95 (q, 1 H, ½ *CH$_2$*–CH$_2$–NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 150.54 (C-2, imidazole), 135.83 (C-1′, C$_6$H$_5$), 132.79 (C-4, imidazole), 128.51, 123.93 (C$_{o,m}$, C$_6$H$_5$), 125.38 (C$_p$, C$_6$H$_5$), 113.42 (C-5, imidazole), 40.01 (CH$_2$–NH), 30.34 (*CH$_2$*–CH$_2$–NH) ppm.

***N*,*N*′-Bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)-ethylenediamine (5a):** Acetylacetone (0.43 mL, 0.42 g, 4.20 mmol) was slowly added to a suspension of *N*,*N*′-bis(1-amino-4-*tert*-butylimidazol-2-yl)ethylenediamine monohydrate (0.74 g, 2.10 mmol) in acetic acid (6 mL). The reaction mixture was refluxed for 4 h, and turned into a red colour. After removal of the solvent, water was added to the viscous product. The resulting orange solid was recrystallised from ethanol and orange crystals were obtained. Yield 0.44 g (52%), m.p. 153 °C. $C_{26}H_{38}N_8$ (462.62): calcd. C 67.50, H 8.28, N 24.22; found C 67.52, H 8.53, N 24.44. ^{1}H NMR (CDCl$_3$): δ = 6.06 (s, 1 H, H-3, imidazopyridazine), 5.36 (br. s, 1 H, NH), 4.16 (s, 2 H, CH$_2$), 2.81 (s, 3 H, CH$_3$–C-4), 2.51(s, 3 H, CH$_3$–C-2), 1.76 [s, 9 H, –C(CH$_3$)$_3$] ppm. ^{13}C NMR (CDCl$_3$): δ = 150.84 (C-7, imidazopyridazine), 141.64 (C-2, imidazopyridazine), 138.71 (C-4, imidazopyridazine), 138.55 (C-4a, imidazopyridazine), 116.76 (C-5, imidazopyridazine), 110.63 (C-3, imidazopyridazine), 44.35 (CH$_2$), 33.57 [–*C*(CH$_3$)$_3$], 32.85 [–C*(CH$_3$)$_3$*], 23.64 (*CH$_3$*–C-4), 21.47 (*CH$_3$*–C-2) ppm.

***N*,*N*′-Bis(2-methyl-4-phenyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (5b):** A stirred suspension of *N*,*N*′-bis(1-amino-4-*tert*-butylimidazol-2-yl)ethylenediamine monohydrate (0.50 g, 1.42 mmol) and benzoylacetone (0.46 g, 2.84 mmol) in acetic acid (5 mL) was refluxed for 1.5 h. The solvent was removed from the red reaction mixture and water was added to the resulting viscous syrup. After recrystallisation from ethanol/chloroform (ratio 2:1) an orange crystalline solid was obtained. Yield 0.54 g (65%), m.p. 260 °C. $C_{36}H_{42}N_8$ (586.75): calcd. C 73.69, H 7.22, N 19.10; found C 73.61, H 7.15, N 19.08. ^{1}H NMR (CDCl$_3$): δ = 7.32–7.25 (m, 5 H, C$_6$H$_5$), 5.65 (s, 1 H, H-3, imidazopyridazine), 5.09 (br. s, 1 H, NH), 3.83 (s, 2 H, CH$_2$), 2.19 (s, 3 H, *CH$_3$*–C-2), 0.93 [s, 9 H, –C*(CH$_3$)$_3$*] ppm. ^{13}C NMR (CDCl$_3$): δ = 150.72 (C-7, imidazopyridazine), 143.46 (C-2, imidazopyridazine), 142.35 (C-4, imidazopyr-

idazine), 140.90 (C-1′, C_6H_5), 139.48 (C-4a, imidazopyridazine), 129.07, 128.56 ($C_{o,m}$, C_6H_5), 128.80 (C_p, C_6H_5), 115.43 (C-5, imidazopyridazine), 111.43 (C-3, imidazopyridazine), 44.31 (CH_2), 33.99 [–*C*$(CH_3)_3$], 31.85 [–C*(CH₃)₃*], 21.61 (*CH₃*–C-2) ppm.

***N*,*N*′-Bis(2,4-dimethyl-5-phenylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (5c):** Acetylacetone (0.28 mL, 0.27 g, 2.68 mmol) was added to a suspension of *N*,*N*′-bis(1-amino-4-phenylimidazol-2-yl)-ethylenediamine (0.50 g, 1.34 mmol) in acetic acid (20 mL). The reaction mixture was stirred and refluxed for 2 h and then turned into a red colour. After removal of the solvent and addition of water an orange solid was obtained and recrystallised from ethanol. Yield 0.35 g (52%), m.p. 231 °C. $C_{30}H_{30}N_8$ (502.60): calcd. C 71.69,H 6.02, N 22.30; found C 71.45, H 6.23, N 22.19. ^{1}H NMR ($CDCl_3$): δ = 7.58–7.26 (m, 5 H, C_6H_5), 5.87–5.86 [d, 1 H, ^4J(H,H) = 3 Hz, H-3, imidazopyridazine], 5.25 (br. s, 1 H, NH), 3.96–3.94 (d, 2 H, *CH₂*–NH), 2.23 (s, 3 H, *CH₃*–C-2), 2.15–2.14 (d, 3 H, $^4J_{H,H}$ = 3 Hz, *CH₃*–C-4) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.39 (C-7, imidazopyridazine), 143.61 (C-2, imidazopyridazine), 138.86 (C-4, imidazopyridazine), 136.08 (C-1′, C_6H_5), 130.32, 127.78 ($C_{o,m}$, C_6H_5), 128.55 (C-4a, imidazopyridazine), 126.88 (C_p, C_6H_5), 117.56 (C-5, imidazopyridazine), 111.33 (C-3, imidazopyridazine), 43.74 (CH_2), 21.35 (*CH₃*–C-2), 19.44 (*CH₃*–C-4) ppm.

***N*,*N*′-Bis(2,4-dimethyl-5-phenylimidazo[1,5-*b*]pyridazin-7-yl)-1,3-diaminopropane Hemihydrate (5d):** Acetylacetone (0.09 mL, 0.09 g, 0.84 mmol) was added to a stirred suspension of *N*,*N*′-bis(1-amino-4-phenylimidazol-2-yl)-1,3-diaminopropane hemihydrate (0.17 g, 0.43 mmol) in acetic acid (5 mL). The reaction mixture was refluxed for 2 h and turned into a red colour. After removal of the solvent and addition of water an orange solid was obtained and recrystallised from ethanol. Yield 0.14 g (62%), m.p. 163 °C. $C_{31}H_{32}N_8 \cdot ½H_2O$ (525.62): calcd. C 70.83, H 6.33, N 21.32; found C 70.62, H 6.15, N 21.39. ^{1}H NMR ($CDCl_3$): δ = 7.48–7.46 (d, 2 H, H_o, C_6H_5), 7.29–7.25 (t, 2 H, H_m, C_6H_5), 7.22–7.18 (t, 1 H, H_p, C_6H_5), 5.79 (s, 1 H, H-3, imidazopyridazine), 5.19 (br. s, 1 H, NH), 3.68 (br. s, 2 H, *CH₂*–NH), 2.14 (s, 3 H, CH_3–C-2), 2.06 (s, 3 H, CH_3–C-4), 2.05–1.98 (m, 1 H, *0,5CH₂*–CH_2–NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.84 (C-7, imidazopyridazine), 144.16 (C-2, imidazopyridazine), 139.31 (C-4, imidazopyridazine), 136.44 (C-1′, C_6H_5), 130.79, 128.17 ($C_{o,m}$, C_6H_5), 128.84 (C-4a, imidazopyridazine), 127.30 (C_p, C_6H_5), 117.92 (C-5, imidazopyridazine), 111.78 (C-3, imidazopyridazine), 40.69 (CH_2–NH), 31.46 (*CH₂*–CH_2–NH), 21.78 (*CH₃*–C-2), 19.85 (*CH₃*–C-4) ppm.

***N*,*N*′-Bis(2-methyl-4,5-diphenylimidazo[1,5-*b*]pyridazin-7-yl)-1,3-diaminopropane Ethanol (5e):** *N*,*N*′-Bis(1-amino-4-phenylimidazol-2-yl)-1,3-diaminopropane hemihydrate (0.40 g, 1.01 mmol) and benzoylacetone (0.33 g, 2.02 mmol) in acetic acid (3 mL) were refluxed whilst stirring. After 1.5 h the solvent was removed from the red reaction solution. Water was added to the resulting highly viscous syrup, which yielded a red solid that was recrystallised from ethanol and red crystals were obtained. Yield 0.56 g (81%), m.p. 180 °C. $C_{41}H_{36}N_8 \cdot C_2H_5OH$ (686.81): calcd. C 75.19, H 6.16, N 16.32; found C 75.09, H 5.97, N 16.46. ^{1}H NMR ($CDCl_3$): δ = 7.17–6.85 (m, 10 H, 2×C_6H_5), 5.97–5.96 (d, 1 H, $^4J_{H,H}$ = 1 Hz, H-3, imidazopyridazine), 5.35 (br. s, 1 H, NH), 3.77–3.76 (d, 2 H, *CH₂*–NH), 3.60–3.55 (m, 1 H, CH_2, ½ C_2H_5OH), 2.25–2.24 (d, 3 H, $^4J_{H,H}$ = 1 Hz, CH_3–C-2), 2.12–2.06 (m, 1 H, *CH₂*–CH_2–NH), 1.13–1.09 (m, 1.5 H, CH_3, ½ C_2H_5OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.87 (C-7, imidazopyridazine), 144.67 (C-2, imidazopyridazine), 142.81 (C-4, imidazopyridazine), 136.39 (C-1′, C_6H_5–C-5), 135.47 (C-1′, C_6H_5–C-3), 129.93, 128.78, 128.39, 127.49 ($C_{o,m}$, 2×C_6H_5), 129.40 (C-4a, imidazopyridazine), 129.11, 126.37(C_p, 2×C_6H_5), 115.51 (C-5, imidazopyridazine), 111.76 (C-3, imidazopyridazine), 58.69 (CH_2, C_2H_5OH), 40.76 (CH_2–NH), 31.49 (*CH₂*–CH_2–NH), 21.98 (*CH₃*–C-2), 18.84 (CH_3, C_2H_5OH) ppm.

***N*,*N*′-Bis{2,4-dimethyl-5-(4-methylphenyl)imidazo[1,5-*b*]pyridazin-7-yl}-1,3-diaminopropane Hemihydrate (5f):** Acetylacetone (0.47 mL, 0.46 g, 4.56 mmol) was added to a stirred solution of *N*,*N*′-bis[1-amino-4-(4-methylphenyl)imidazol-2-yl]-1,3-diaminopropane (0.95 g, 2.28 mmol) in acetic acid (15 mL). The reaction mixture was refluxed for 2 h and turned into a red colour. The solvent was removed under reduced pressure. Water was added to the resulting red highly viscous syrup and gave an orange solid, which was recrystallised from ethanol/water (ratio 2:1). Yield 1.07 g (85%), m.p. 180 °C. $C_{33}H_{36}N_8 \cdot ½H_2O$ (553.67): calcd. C 71.58, H 6.74, N 20.24; found C 71.63, H 6.88, N 20.15. ^{1}H NMR ($CDCl_3$): δ = 7.36–7.34 (d, 2 H, H_o, C_6H_4), 7.08–7.06 (d, 2 H, H_m, C_6H_4), 5.75 (s, 1 H, H-3, imidazopyridazine), 5.18 (br. s, 1 H, NH), 3.66–3.65 (bd, 2 H, *CH₂*–NH), 2.27 (s, 3 H, *CH₃*–C_6H_4), 2.12 (s, 3 H, *CH₃*–C-2), 2.05 (s, 3 H, *CH₃*–C-4), 2.02–1.96 (m, 1 H, ½ *CH₂*–CH_2–NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.80 (C-7, imidazopyridazine), 144.06 (C-2, imidazopyridazine), 139.40 (C-4, imidazopyridazine), 136.91 (*C*–CH_3, C_6H_4), 133.53 (C-1′, C_6H_4), 130.67, 128.88 ($C_{o,m}$, C_6H_4), 128.94 (C-4a, imidazopyridazine), 117.76 (C-5, imidazopyridazine), 111.50 (C-3, imidazopyridazine), 40.69 (*CH₂*–NH), 31.48 (*CH₂*–CH_2–NH), 21.73 (*CH₃*–C-2), 21.68 (*CH₃*–C_6H_4), 19.83 (*CH₃*–C-4) ppm.

Complex Synthesis

Preparation of 6: A solution of bis(dimethylamino)titanium dichloride (0.22 g, 1.08 mmol) in diethyl ether (20 mL) was slowly added to a stirred orange solution of *N*,*N*′-bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (0.50 g, 1.08 mmol) in diethyl ether (30 mL) and the reaction mixture turned into a dark violet colour. After stirring for 16 h the solvent was removed under vacuum. The residue was washed with 5 mL of hexane. The violet product was dried in vacuo. A concentrated solution of diethyl ether at –30 °C gave X-ray diffraction quality crystals. Yield 0.58 g (92%). $C_{26}H_{36}Cl_2N_8Ti$ (579.38): calcd. C 53.90, H 6.26, N 19.34; found C 54.43, H 6.48, N 19.66. ^{1}H NMR ([D_8]THF): δ = 6.25–6.24 (d, 1 H, $^4J_{H,H}$ = 1 Hz, H-3, imidazopyridazine); 4.99 (s, 2 H, *CH₂*–CH_2); 2.77 (s, 6 H, 2×CH_3); 1.56[s, 9 H, -C*(CH₃)₃*] ppm. ^{13}C NMR ([D_8]THF): δ = 153.46 (C-7, imidazopyridazine); 147.75(C-2, imidazopyridazine); 142.57, 142.03 (C-4, C-4a, imidazopyridazine); 124.46(C-5, imidazopyridazine); 109.86 (C-3, imidazopyridazine); 57.23 (*CH₂*–CH_2); 34.08 [–*C*$(CH_3)_3$]; 31.70 [–C*(CH₃)₃*]; 22.41 (*CH₃*–C-2); 20.63 (*CH₃*–C-4) ppm.

Preparation of 7: Tetrakis(diethylamino)zirconium (0.20 mL, 0.21 g, 0.54 mmol) was slowly added, via a syringe, to a stirred orange solution of *N*,*N*′-bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]-pyridazin-7-yl)ethylenediamine (0.25 g, 0.54 mmol) in diethyl ether (25 mL). The resulting dark violet reaction mixture was stirred for 3.5 h at room temperature. The solution was concentrated to 10 mL. After cooling to –78 °C dark violet crystals were obtained. The solution was decanted, concentrated and at –30 °C more crystalline product was obtained. The crystals were collected and dried under vacuum. Yield 0.27 g (73%), m.p. 236 °C. $C_{34}H_{56}N_{10}Zr$ (696.08): calcd. C 58.66, H 8.11, N 20.12; found C 57.41, H 8.01, N 19.74. ^{1}H NMR ([D_8]THF): δ = 5.77–5.76 (d, 1 H, $^4J_{H,H}$ = 1 Hz, H-3, imidazopyridazine), 4.14 (s, 2 H, *CH₂*–CH_2), 3.07–2.99 [q, 4 H, –*N*–(*CH₂*–CH_3)$_2$], 2.57–2.56 (d, 3 H, $^4J_{H,H}$ = 1 Hz, CH_3–C-4), 2.48(s, 3 H, CH_3–C-2), 1.47 [s, 9 H, –C*(CH₃)₃*], 0.57–0.51 [t, 6 H, (*CH₃*–CH_2)$_2$–*N*–] ppm. ^{13}C NMR ([D_8]THF): δ = 153.23 (C-7, imidazopyridazine), 149.02(C-2, imidazopyridazine), 143.70 (C-4, imidazopyridazine), 141.50 (C-4a, imidazopyridazine), 117.12 (C-5, imidazopyridazine), 107.60 (C-3, imidazopyridazine), 52.47

(CH_2–CH_2), 43.24 [–N–(CH_2–CH_3)$_2$], 33.82 [–C(CH_3)$_3$], 31.97 [–C$(CH_3)_3$], 22.45 (CH_3–C-4), 20.83 (CH_3–C-2), 14.29 (CH_3–CH_2)$_2$–N–) ppm.

Preparation of 8: *n*BuLi (1.21 mL, 3.02 mmol, 2.5 M in hexane) was slowly added to a stirred solution of *N*,*N*′-bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (0.70 g, 1.51 mmol) in THF (10 mL) at –60 °C. After complete addition, the dark blue mixture was stirred for 1.5 h at –60 °C and warmed to –40 °C. At this temperature a suspension of [$CrCl_3$(THF)$_3$] (0.57 g, 1.51 mmol) in THF (10 mL) was added. The resulting dark green reaction mixture was stirred for 30 min at –40 °C and warmed to room temperature and stirred for a further 24 h. The solution was concentrated to ¼ of its volume and 30 mL of diethyl ether was added. The mixture was filtered, the residue washed with 10 mL of diethyl ether and 10 mL of hexane. The combined filtrates were concentrated to 15 mL. By cooling to –30 °C a dark green/blue crystalline product was obtained. Yield 0.57 g (69%), m.p. 307 °C. $C_{52}H_{72}Cl_2Cr_2N_{16}$ (1096.10): calcd.C 56.98, H 6.62, N 20.45; found C 57.42, H 7.11, N 20.02. μ_{eff} = 4.28 μ_B.

Preparation of 9: A solution of *N*,*N*′-bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (0.70 g, 1.51 mmol) in THF (20 mL) was cooled to –78 °C. *n*BuLi (1.88 mL, 3.02 mmol, 1.6 M in hexane) was slowly added to this stirred solution via a syringe. The resulting dark blue reaction mixture was stirred for 30 min at –78 °C and then warmed to room temperature. After stirring for 30 min a solution of chloro-1,5-cyclooctadieneiridium(I) dimer (1.01 g, 1.51 mmol) in THF (30 mL) was added at 0 °C. The resulting dark green reaction mixture was stirred for 18 h at room temperature. The solution was concentrated to ¼ of its volume and 30 mL of dichloromethane was added. The mixture was filtered and the filtrate concentrated to dryness under vacuum. The resulting residue was recrystallised from toluene and dark green crystals were collected at –30 °C. Yield 1.34 g (84%), $C_{42}H_{60}Ir_2N_8$ (1061.38): calcd. C 47.52, H 5.70, N 10.56; found C 48.02, H 5.82, N10.83. ^{1}H NMR (CD_2Cl_2): δ = 5.62–5.61 (d, 1 H, $^4J_{H,H}$ = 1 Hz, H-3, imidazopyridazine), 4.51 (br. s, 2 H, 2×CH, COD), 4.32 (br. s, 2 H, 2×CH, COD), 3.80 (s, 2 H, CH_2–N), 2.58–2.57 (d, 3 H, $^4J_{H,H}$ = 1 Hz, CH_3–C-4), 2.36 (s, 3 H, CH_3–C-2), 2.24–2.11 (m, 4 H, 2×CH_2, COD), 1.77–1.66 (m, 4 H, 2×CH_2, COD), 1.48 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (CD_2Cl_2): δ = 159.88 (C-7, imidazopyridazine), 155.07 (C-2, imidazopyridazine), 149.71 (C-4, imidazopyridazine), 139.98 (C-4a, imidazopyridazine), 119.34 (C-5, imidazopyridazine), 108.56 (C-3, imidazopyridazine), 62.09 (2×CH, COD), 51.21 (2×CH, COD), 47.55 (CH_2–N), 34.98 [C(CH_3)$_3$], 31.71 [C$(CH_3)_3$], 31.64 (2×CH_2, COD), 30.64 (2×CH_2, COD), 23.10 (CH_3–C-2), 20.35 (CH_3–C-4) ppm.

Preparation of 10: A solution of *N*,*N*′-bis(2,4-dimethyl-5-*tert*-butylimidazo[1,5-*b*]pyridazin-7-yl)ethylenediamine (0.50 g, 1.08 mmol) in THF (10 mL) was cooled to –78 °C. *n*BuLi (0.86 mL, 2.16 mmol, 2.5 M in hexane) was slowly added to this stirred solution via a syringe. The resulting dark blue reaction mixture was stirred for 30 min at –78 °C and then warmed to room temperature. After stirring for 30 min a suspension of chloro-1,5-cyclooctadienerhodium(I) dimer (0.54 g, 1.08 mmol) in THF (20 mL) was added. The resulting dark green reaction mixture was stirred for 18 h at room temperature. The solution was concentrated to ⅓ of its volume and 30 mL of diethyl ether was added. The mixture was filtered and the precipitate was washed twice with 10 mL of diethyl ether. The combined filtrates were concentrated to dryness under vacuum. Crystals of **10** were grown from toluene at –30 °C. Yield 0.51 g (54%), m.p. 275 °C. $C_{42}H_{60}N_8Rh_2$ (882.78): calcd. C 57.14, H 6.85, N 12.69; found C 57.62, H 7.21, N 12.27. ^{1}H NMR (CD_2Cl_2): δ = 5.46 (s, 1 H, H-3, imidazopyridazine); 4.60 (br. s, 4 H, 4×CH, COD); 3.30 (s, 2 H, CH_2–N); 2.50 (s, 3 H, CH_3–C-4); 2.39–2.35 (m, 4 H, 2×CH_2, COD); 2.15 (s, 3 H, CH_3–C-2); 1.89–1.83 (m, 4 H, 2×CH_2, COD); 1.43 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C NMR (CD_2Cl_2): δ = 156.50 (C-7, imidazopyridazine); 152.47 (C-2, imidazopyridazine); 146.50 (C-4, imidazopyridazine); 138.74 (C-4a, imidazopyridazine); 116.98 (C-5, imidazopyridazine); 106.55 (C-3, imidazopyridazine); 77.24, 77.13, 69.62, 69.53 (4×CH, COD); 46.58 (CH_2–N); 33.46 [C(CH_3)$_3$]; 31.35 [C$(CH_3)_3$]; 30.21 (2×CH_2, COD); 29.74 (2×CH_2, COD); 22.01 (CH_3–C-2); 19.00 (CH_3–C-4) ppm.

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