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Synthesis of Ligands Based on 4*H*-Imidazoles and Pyridine Subunits: Selective Complexation and Bathochromically Absorbing Complexes

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New multifunctional ligands based on the combination of 4*H*-imidazoles with pyridine subunits have been synthesised. The long wavelength absorptions originating from the merocyanine-chromophore can be shifted towards the near infrared (NIR) region by introduction of additional auxochromic groups. Due to different complexation spheres these hybrid-ligands form the requirements for the construction of heterobimetallic complexes. In addition, the hybrid ligands are redox active compounds showing two separated fully reversible reductions.

Introduction

Coordination chemistry plays a fundamental role in supramolecular chemistry.[1] Among other chelating agents, oligopyridines and other 1,4-diazadienes in the coordination of metal-containing building blocks have attracted special interest.

With respect to the conversion of solar energy, dyads, triads and other arrangements in which an antenna molecule is connected with an electron-accepting part have become increasingly important as they allow for directional energy transfer.[2] For example, bi- and terpyridine complexes of several metals are often part of such supramolecular architectures.[3] Besides oligopyridines, metal complexes of other azaheterocycles[4–9] have become of increasing importance. The construction of architectures aimed at converting light energy into chemical energy or information requires the use of multifunctional well understood building blocks. An illustrative example of the implementation of these design principles is the Eu^{III} cryptate in which the hexapyridodiaza cryptate serves not only as a ligand for the europium ion but also as a UV-antenna, absorbing light energy and transferring it to the Eu^{III} centre. The sensitised transition at the europium results in emission of light from the metal centre.[10]

The dual function of the ligand is clearly evident in this example. However, these azaheterocycles only absorb in the ultraviolet region which seriously impedes application of the so formed photochemical molecular device since this energy rich radiation damages biological matter and leads to different photochemical reactions such as bond cleavage. It is therefore highly desirable to retain the well documented ligand properties of 1,4-diazadienes and introduce new chromophoric properties into this ligand system. Recently, details of optimised ligands for the construction of dye-sensitised solar cells were published,[11] the latter showing intense absorptions in a broad range of the spectra.

To the best of our knowledge, oligopyridines which possess an additional functional dye substructure are quite rare to date.[12] There is still a need to integrate functional chromophoric systems into pyridines/oligopyridines. Moreover, especially for the application of light driven energy conversion on a molecular level, storage and triggered release of redox equivalents within a molecular subunit are extremely important properties as they facilitate the two electron reduction of protons to molecular hydrogen even in systems containing only one photo-redox active one-electron transfer agent such as a Ru(bpy)$_3$$^{2+}$ unit.[5] The 4*H*-imidazoles **1** (Figure 1) for which different syntheses[13] were developed

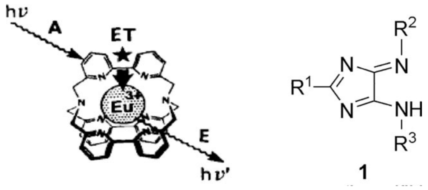

Figure 1. Principle of a UV-antenna and structure of "chromophore-ligands" of type of 4*H*-imidazoles **1**.

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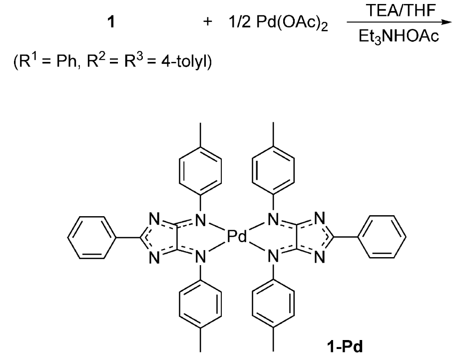
in our group are unique substances which fulfil these criteria:

- The protonation/deprotonation is connected with a drastic alteration of colour due to the change of the chromophore [cyanine-merocyanine-(aza)oxonole].[14]
- Absorption of visible light ($\lambda_{\max}$ up to 580 nm) with high extinction coefficients (ε up to 4.5).
- Reversible two-electron redox systems,[15a,15b] in cyclised form (boratetraazapentalenes), the corresponding radical anion (SEM-form) shows unusual high K_{SEM} values (up to 10^{15}).[16]
- The peripheral 1,4-diamino/imino substructures present good prerequisites for the construction of metal chelate complexes; the recently reported Pd complexes proved to be electrochemically active.[17c]

Due to the last fact, the combination of oligopyridines with 4*H*-imidazoles might result in two different coordination spheres. Such types of ligands offer some advantages for the construction of heterobimetallic complexes and for supramolecular structures. Recently, the value of such types of complexes in generating hydrogen has been clearly demonstrated.[5] Obviously, the bridging ligand can be regarded as key-part in such compounds. In the following part, the syntheses and the properties of some new multifunctional ligands are presented.

Results and Discussion

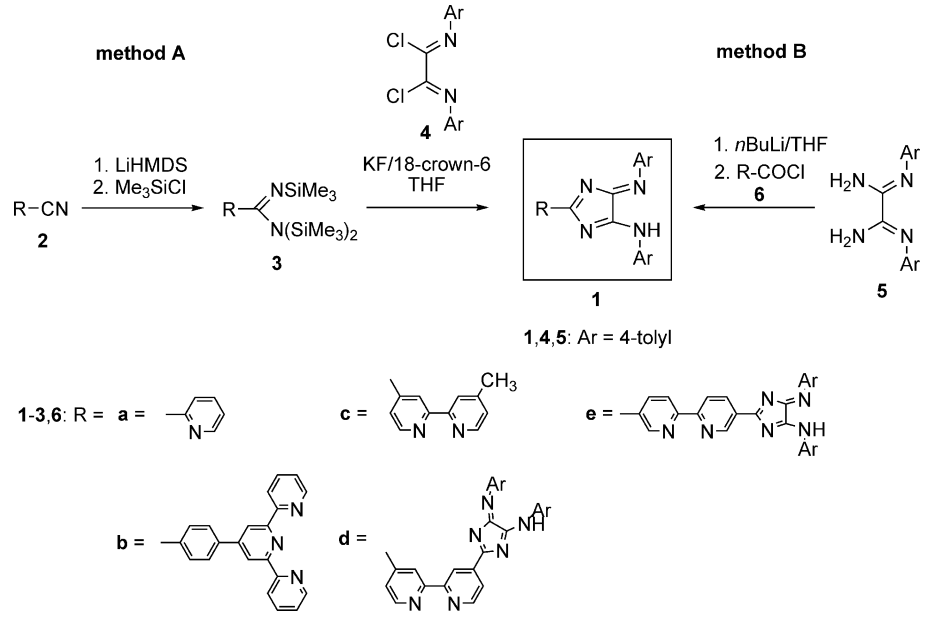
In addition to the Pd complexes mentioned above[17c] we also succeeded in synthesising an appropriate palladium complex consisting of two chelating 4*H*-imidazoles. Compared with the analogous Pd^{II}-allyl complex,[17c] **1-Pd** shows a bathochromic shift of 30 nm to 630 nm. The synthetic route is depicted in Scheme 1. In contrast to an analogous Zn complex,[17b] this Pd complex has good solubility in most common solvents and could, therefore, be characterised completely.



Scheme 1. Synthesis of the (4*H*-imidazol)$_2$-Pd complex **1-Pd**.

For the synthesis of novel multifunctional ligand systems, two different methods were employed (Scheme 2). Method A[13] starts from the appropriate nitrile/dinitrile **2** whereas in method B[18] carboxylic acid chlorides **6** serve as building blocks. Reactions of the nitriles **2** with lithium hexamethyldisilazide (LiHMDS) yielded the corresponding amidinates which were converted into the persilylated amidines by heating with chlorotrimethylsilane under reflux. Finally, the 4*H*-imidazoles of type **1** were obtained by a deprotection-cyclisation sequence of the persilylated amidines using bis(imidoyl chlorides) **4** in the presence of KF/18-crown-6. Alternatively, in method B,[18] the cyclisation reaction between oxalamidines **5** and carboxylic acid chlorides **6** formed the desired products.

Recently, we reported the synthesis of the pyridyl-substituted 4*H*-imidazole **1a** (R = 2-pyridyl, Ar = 4-tolyl)[13c] starting from the commercially available pyridyl-2-carb-



Scheme 2. Two synthetic pathways to 4*H*-imidazoles **1**.

amidine. Its synthesis has now been improved using cheaper 2-cyanopyridine as the starting material. The conversion into the corresponding imidoester derivative (NaOMe/methanol) and subsequent aminolysis reaction with ammonium chloride gave the amidine in high yield (93%) which was finally cyclised according to method A to yield **1a**. In an adapted synthesis starting from nitriles **2b** and **2d**, derivatives **1b** and **1d** can be isolated in medium yields.

For the preparation of **1c** and **1e**, the commercially available carboxylic/dicarboxylic acids formed the basis. Upon treatment with thionyl chloride in the presence of small amounts of DMF they were converted into the corresponding acid chlorides **6c** and **6e**. The 4*H*-imidazoles **1c** and **1e** were formed by slow addition of **6c/e** to a THF solution containing the deprotonated (*n*BuLi) oxalamidine **5** (method B). The immediate formation of the products (as anions) can be followed visually by the abrupt colour change from yellow to deep purple. After work-up and purification by column chromatography both 4*H*-imidazoles were obtained in yields of about 50%. All new synthesised derivatives **1a**–**e** are air-stable red microcrystalline compounds. The spectroscopic data are in agreement with their structures. Besides the characteristic patterns of fragmentation, the M^+ peak could clearly be detected in the mass spectra of all compounds. Due to the high symmetry in the molecules of **1b**, **1d**, **1e** and **1f**, the ^1H NMR spectra feature single sets of signals. The aromatic protons of the tolyl groups form the characteristic AB-system and can be easily detected as two separated doublets. In derivatives **1b** and **1f** the protons of the terpyridine subunits are characteristically shifted towards low field.

The easy protocol according to method B gave rise to an improvement in the synthesis of derivative **1a** making this way the method of choice. Starting from picolinic acid chloride, derivative **1a** can be obtained in a yield of 50%.

Figure 2 shows the absorption and emission spectra of derivatives **1b** und **1e** in their neutral, protonated as well as deprotonated forms. As depicted in this figure, all new synthesised derivatives display, in solution, strong absorptions in the region between 300 and 550 nm. Protonation/deprotonation causes an alteration of their chromophoric systems and consequently of their long wavelength absorption in their UV/Vis spectra. Compared with the neutral species, both the protonated (cyanine) and the deprotonated 4*H*-imidazole (azaoxonole) display a bathochromic shift in their UV/Vis spectra.

In order to achieve a stronger bathochromic shift for the neutral state, the introduction of auxochromic substituents was tested next. This objective could be realised by an exchange of peripheral arylic substituents in the merocyanine system of compounds **1**.[13b,14] Thus, the novel 4*H*-imidazole **1f** (formula **1b**, Ar = $4\text{-Me}_2\text{N-C}_6\text{H}_4$) was obtained by replacement of both tolyl residues by a transamination reaction of **1b** with 4-(dimethylamino)aniline (Scheme 3). Derivative **1f** was isolated in the form of a black-bluish powder which is soluble in THF giving a strong blue colour. As expected, in the UV/Vis-spectrum of **1f**, the introduction of auxochromic groups caused a bathochromic shift of about 100 nm (Figure 3). This successful transformation may open the way for obtaining novel ligands showing NIR-absorptions.[15b]

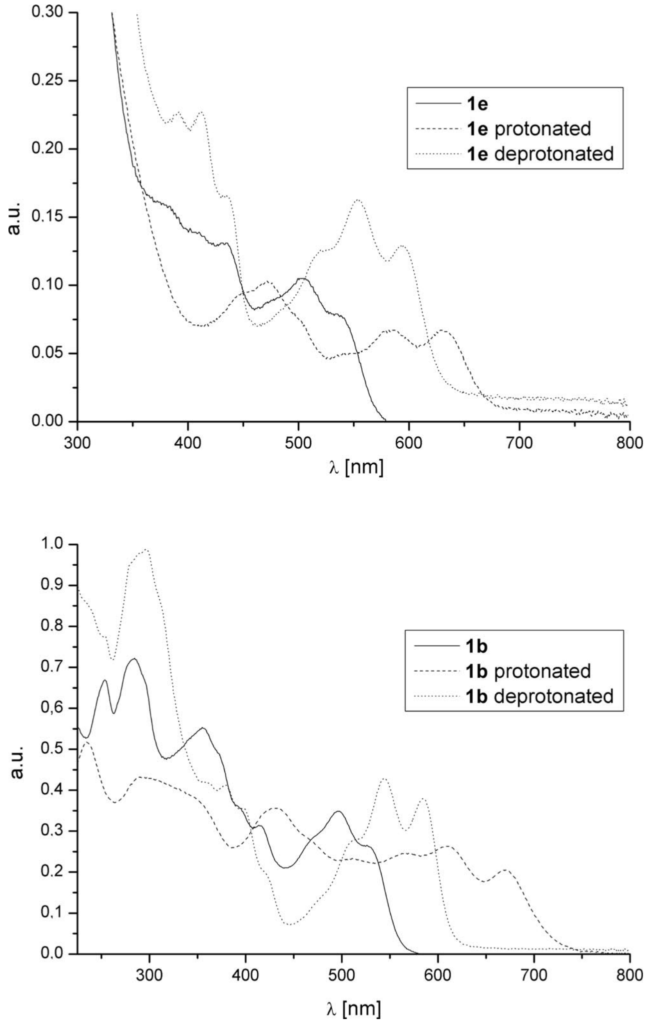
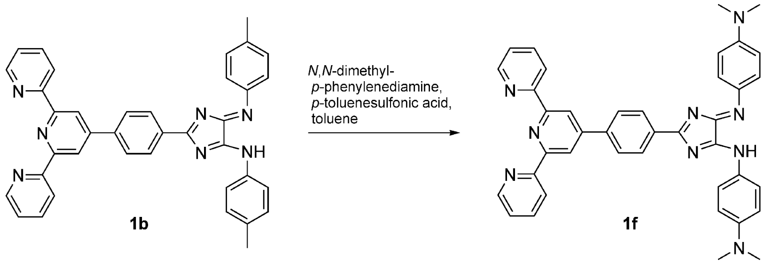


Figure 2. UV/Vis-spectra of **1e** and **1b**.

According to previous findings, 4*H*-imidazoles proved to be reversible two-electron redox systems.[15a,15b,16] In addition to the pH dependence of their UV/Vis spectra, their electrochemical behaviour was studied. Exemplified by compound **1b** for mono-4*H*-imidazoles, electrochemical measurements were performed. The reduction of **1b** occurred in two steps ($U_1^{1/2}$ = –0.815 V, $U_2^{1/2}$ = –1.465 V; $K_{\text{SEM}} = 1.04 \times 10^{11}$).

Recently, new palladium complexes of simple 4*H*-imidazols were synthesised and fully characterised.[17c] Based on these findings, some of the ligands described here were tested with respect to their selective coordination behaviour.

The model reaction between ligand **1a** and allyl-Pd^{II} chloride dimer in THF in the presence of triethylamine gave only the Pd complex **1a-Pd**. In this very fast complexation reaction, the metal coordinated to both peripheral N-atoms of the 4*H*-imidazole as well as at the 1,4-diazadiene resulting from the combination of pyridine-4*H*-imidazole.



Scheme 3. Synthesis of ligand **1f** by means of a transamination reaction.

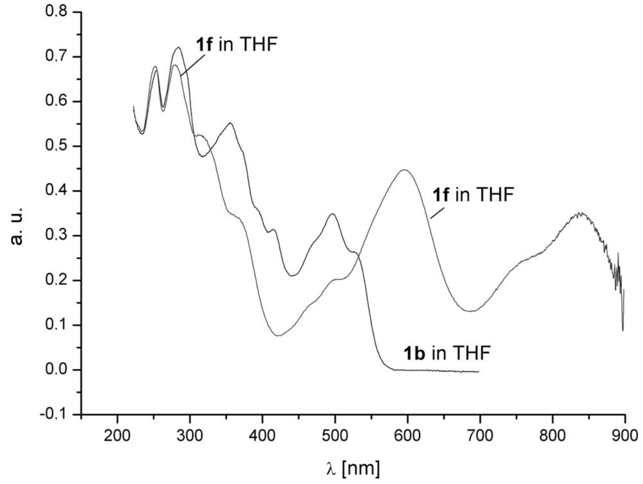
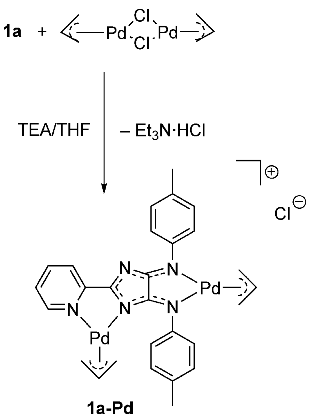


Figure 3. Bathochromic shift of derivative **1f** compared with the parent compound **1b**.

Consequently, the positively charged homobimetallic complex with a chloride as the counterion could be isolated (Scheme 4).



Scheme 4. Synthesis of the complexes **1a-Pd**.

All attempts to differentiate between both complexation spheres, however, failed. In the mass spectrum of **1a-Pd**, the base peak ($m/z = 646$) is consistent with the homobimetallic complex. Its further fragmentation by gradual elimination of both allyl groups and palladium is characteristic for such complexes and can easily be seen in the spectrum. Furthermore, the existence of these two different allyl ligands was confirmed by NMR experiments in the course of which an unambiguous assignment was possible. The UV/Vis spectrum of **1a-Pd** is very similar to those of other palladium complexes of 4*H*-imidazoles featuring a strong absorption maximum at 560 nm (Figure 4).

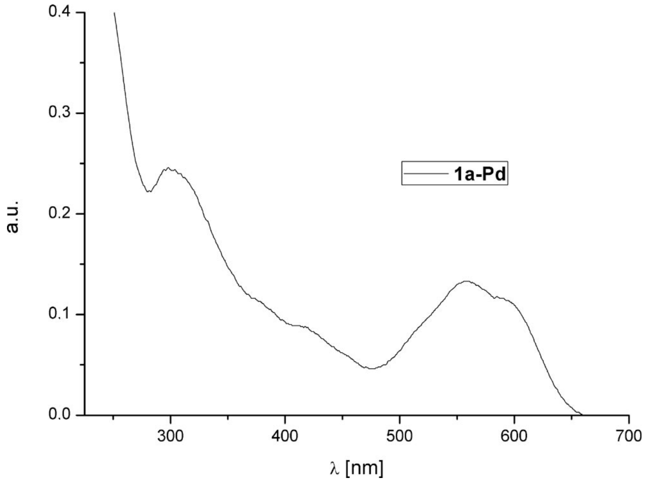
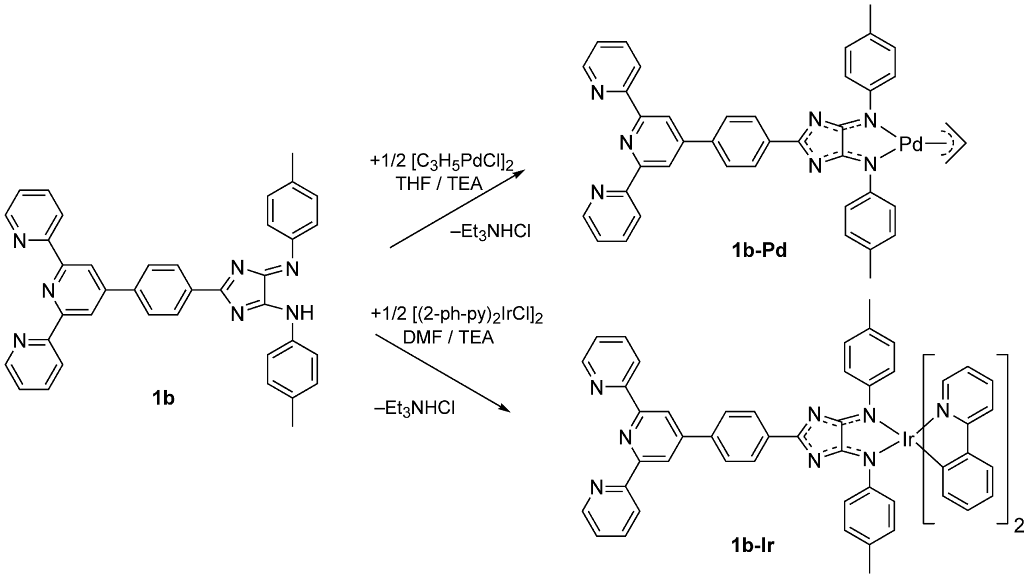


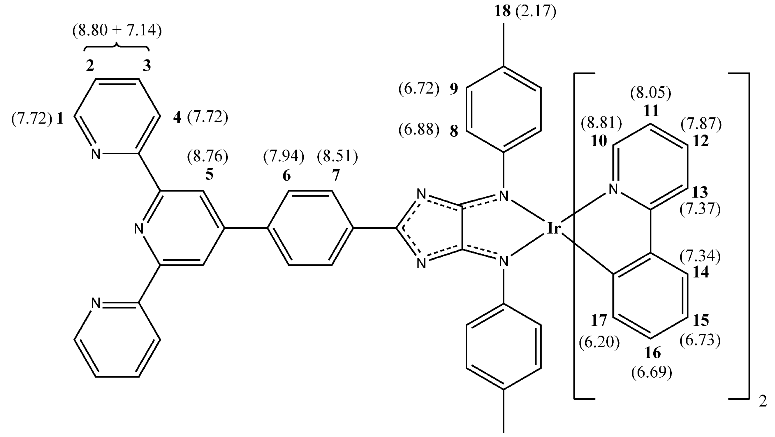
Figure 4. UV/Vis-spectrum of complex **1a-Pd**.

Ligand **1b** in which the terpyridine subunit is in competition with the chelating sphere of the 4*H*-imidazole was the next promising ligand for the construction of heterobimetallic species. In this case we succeeded in differentiating between both chelating spheres. Besides the expected homobimetallic complex, the neutral monopalladium complex **1b-Pd** was isolated as by-product in small amounts (Scheme 5). The structure of this complex was mainly elucidated from its MS and NMR spectroscopic data. The protons of the allyl ligand absorb characteristically in the regions of 5.2–5.8 ppm (CH) and 3.0–4.0 ppm (CH_2). The coordination of the metal at the 4*H*-imidazole unit could be clearly highlighted by NOESY experiments in which the coupling of the *ortho* protons of the aryl substituents with the protons of the CH_2 group of the allyl ligand was detected. No coupling to protons of the terpyridine subunit was observed. These findings demonstrate that the combination of pyridines with 4*H*-imidazoles should, in principle, allow a new entry to heterobimetallic complexes with long wavelength absorptions.

In contrast to palladium, iridium allowed the very selective formation of a monometallic complex **1b-Ir** in which only the 4*H*-imidazole core acted as a chelating ligand sphere (Scheme 5). This complex was obtained in good yield as a brown powder. As expected, the iridium complex



Scheme 5. Synthesis of the complexes **1b-Pd** and **1b-Ir**.



Scheme 6. Assignment of H-atoms 1–18 (shifts in ppm) of **1b-Ir**.

1b-Ir showed a broad absorption in the region between 500 and 650 nm. The ^{1}H NMR spectrum and, in addition, TOCSY-, ROESY-, NOESY- and HSQC-experiments as well as the ^{13}C-NMR spectra, allowed a complete structural determination (Scheme 6). Theoretically, three different isomers can be formed during the reaction i.e. the N,N-*trans*-, the C,N-*trans*- and the C,C-*trans* isomers (with respect to the coordinating atoms of the two phenylpyridine ligands) of **1b-Ir**. Due to the presence of double sets of signals in some cases, it is most likely that two geometrical isomers of **1b-Ir** were formed during the reaction in a ratio of approximately 9:1. The analytical data reported refer to the N,N-*trans*-isomer of **1b-Ir** being the main product (Figure 5).

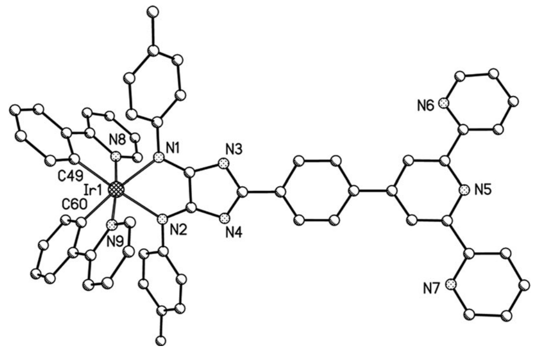


Figure 5. Molecular structure of **1b-Ir** (the H atoms have been omitted for clarity). Selected bond lengths [Å]: Ir–N1 2.173(8), Ir–N2 2.191(9), Ir–N8 2.045(8), Ir–C49 2.000(10), Ir–C60 2.015(11), Ir–N9 2.034(9).

Final and unambiguous proof for the selective complexation reaction was obtained by X-ray structural analysis on a single crystal of complex **1b-Ir** (Figure 5).

Conclusions

Novel multifunctional hybrid-ligands have been prepared based from the combination of pyridines with 4*H*-imidazoles. They are characterised by broad absorptions in their UV/Vis spectra spanning 400–750 nm. The synthesis of complex **1b-Ir** clearly demonstrated that ligands consisting of a terpyridyl substructure and a 4*H*-imidazole are capable of acting as selective and multifunctional ligands. In this case, only the N-ligand atoms of the 4*H*-imidazole were integrated into the complex formation with a catalytically active metal such as iridium. Depending on the number of 4*H*-imidazoles, ligands were synthesised which are capable of binding two or three metal centres. The syntheses and properties of further metal complexes, applicable as antenna parts in light-harvesting systems will be the subject of a forthcoming paper.

Experimental Section

General: All reactions were monitored by TLC, carried out on 0.25 mm Merck TLC aluminium sheets (aluminium oxide 150 F_{254} neutral or silica 60 F_{254}) and visualised using UV light. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 (400 MHz) or a Bruker AC 250 (250 MHz) spectrometer. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out in-house with an automatic LECO CHNS 932 analyser.

Synthesis of Hybrid Ligand 1a: Pyridine-2-carbonitrile (0.1 mol, 10.4 g) was dissolved in methanol (100 mL) and NaOMe (0.02 mol, 1.08 g) was added and the solution stirred for 12 h at room temperature. After adding ammonium chloride (0.1 mol, 5.76 g) the reaction mixture was heated under reflux for 3 h. The solution was then evaporated to dryness and the residue suspended in ethanol (100 mL) and heated under reflux for 1 h. The mixture was filtered off and the filtrate was concentrated to 25 mL. The resultant precipitate was recrystallised from 2-propanol/*n*-pentane to yield 11.26 g (93 %) of pyridine-2-carbamidine.

Pyrdidine-2-carbamidine (1 mmol, 121 mg) and bis(imidoyl chloride) **4** (1 mmol) were dissolved in THF (100 mL) in the presence of triethylamine (2 mmol, 0.28 mL) and the reaction mixture was heated under reflux for 6 h. The reaction mixture was evaporated to dryness and the residue suspended in CH_2Cl_2. The filtrate was again evaporated to dryness and purified by column chromatography (alumina, activity V, toluene at the beginning, then toluene/ethanol, 1:1); yield 190 mg (54 %). Analytical data were in agreement with those reported.[13c]

General Procedure for the Synthesis of Hybrid Ligands 1a, 1b, 1d: To a suspension of the corresponding nitrile **2a**, **2b**, **2d** (1 mmol) in THF (5 mL) in a Schlenk tube **2a**, **2b** (1 mL) or **2d** (2 mL) as a 1 M lithium hexamethyldisilazide solution (in THF) was added dropwise. The reaction mixture was then stirred for 4 d at room temperature. The solution was evaporated to dryness and the residue was suspended in toluene. Chlorotrimethylsilane (1 mmol, 0.13 mL for **2a**, **2b** or 1 mmol, 0.13 mL for **2a**, **2b**) was added and the reaction mixture was heated under reflux for 12 h. The mixture was again evaporated to dryness and the remaining residue was treated with bis(imidoyl chloride) **4** (1 mmol, 305 mg for **2a**, **2b** or 2 mmol, 610 mg for **2d**) in the presence of KF/18-crown-6 (3 mmol, 174 mg/793 mg for **2a**, **2b** or 6 mmol, 349 mg/1586 mg for **2d**) in THF. For the completion of the reaction the mixture was stirred for 24 h at room temperature.

Hybrid Ligand 1b: The reaction mixture was evaporated to dryness and the residue was suspended in warm methanol. The precipitate was filtered off, washed three times with warm methanol and dried in vacuo; yield 262 mg (45 %). ^{1}H NMR (250 MHz, $[D_8]$THF): δ = 8.95 (s, 2 H), 8.73 (m, 6 H), 8.12 (d, 2 H), 8.02 (d, 4 H), 7.93 (t, 2 H), 7.40 (t, 2 H), 7.26 (d, 4 H), 2.39 (s, 6 H) ppm. ^{13}C NMR (63 MHz, $[D_8]$THF): δ = 188.4, 157.2, 156.9, 150.1, 144.3, 137.5, 136.9, 134.2, 133.7, 131.8, 130.2, 128.9, 128.1, 124.8, 121.7, 119.5, 21.2 ppm. MS (DEI): *m*/*z* = 584 $[M + H]^+$, 583 $[M]^+$, 568 $[M - CH_3]^+$. UV/Vis (THF): λ_{max} (lg ε) = 497 nm (4.16), 526 nm (4.04). $C_{38}H_{29}N_7$ (583.66): calcd. C 78.19, H 5.01, N 16.80; found C 77.91, H 5.46, N 16.63.

Hybrid Ligand 1d: The reaction mixture was evaporated to dryness and the residue was suspended in water. The precipitate was filtered off and washed with water. The residue was then washed with methanol until the filtrate was almost colourless and finally washed with *n*-pentane and dried in vacuo; yield 289 mg (41 %). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 9.37 (s, 2 H), 9.00 (d, 2 H), 8.41 (d, 2 H), 7.97 (d, 8 H), 7.35 (d, 8 H), 2.44 (s, 12 H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 187.5, 157.5, 156.8, 150.0, 140.7, 137.5, 135.3, 129.9, 123.8, 120.4, 119.7, 21.0 ppm. MS (DEI): *m*/*z* = 704 $[M]^+$. UV/Vis (THF): λ_{max} (lg ε) = 502 (4.43), 530 nm (4.32). $C_{44}H_{36}N_{10}$ (704.80): calcd. C 74.98, H 5.15, N 19.87; found C 75.09, H 5.30, N 19.61.

General Procedure for the Synthesis of 1c, 1e: In a 100 mL one-necked round-bottom flask, equipped with a magnetic stirrer, the corresponding carboxylic acid (1 mmol) was dissolved or suspended in thionyl chloride (50 mL). A catalytic amount of DMF was added and the reaction mixture was heated under reflux for 2 h. The resultant yellow solution was cooled to room temperature, the solvent was evaporated and the remaining residue dried in vacuo. The acyl chlorides thus formed **6a**, **6c**, **6e** and **6f** were then added to a THF solution containing the deprotonated oxalamidine **5**, yielded by deprotonation of **5** with *n*BuLi (0.8 mL of a 2.5 M solution in *n*-hexane). For the completion of the reaction the mixture was stirred for 20 h at room temperature.

Hybrid Ligand 1c: The reaction mixture was evaporated to dryness and the red compound was purified by column chromatography (alumina, activity V, toluene/acetone, 5:1); yield 196 mg (44 %). ^{1}H NMR (250 MHz, $[D_8]$THF): δ = 9.41 (s, 1 H), 8.82 (d, 1 H), 8.55 (d, 1 H), 8.41 (s, 1 H), 8.30 (d, 1 H), 8.00 (d, 4 H), 7.27 (d, 4 H), 7.18 (d, 1 H), 2.39 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $[D_8]$THF): δ = 187.0, 157.2, 155.6, 149.4, 148.9, 147.5, 140.6, 131.4, 129.4, 124.5, 121.6, 121.2, 120.0, 20.1 ppm. MS (DEI): *m*/*z* = 444 $[M]^+$, 429 $[M - CH_3]^+$. UV/Vis (THF): λ_{max} (lg ε) = 502 (4.0), 532 nm (3.89). $C_{28}H_{24}N_6$ (444.51): calcd. C 75.65, H 5.44, N 18.91; found C 75.21, H 6.02, N 18.77.

Hybrid Ligand 1e: The reaction mixture was evaporated to dryness and the residue suspended in warm methanol. The precipitate was filtered and washed two times with methanol (50 mL). The pure compound was obtained by recrystallisation from THF; yield 411 mg (58 %). ^{1}H NMR (250 MHz, $[D_8]$THF): δ = 9.76 (s, 2 H), 8.89 (d, 2 H), 8.81 (d, 2 H), 8.02 (d, 8 H), 7.28 (d, 8 H), 2.39 (s, 12 H) ppm. MS (DEI): *m*/*z* = 704 $[M]^+$, 703 $[M - H]^+$, 689 $[M - CH_3]^+$. UV/Vis (THF): λ_{max} (lg ε) = 504 (3.60), 535 nm (3.48). $C_{44}H_{36}N_{10}$ (704.80): calcd. C 74.98, H 5.15, N 19.87; found C 74.91, H 5.25, N 19.84.

Synthesis of Hybrid Ligand 1f: Compound **1b** (1 mmol, 584 mg) was suspended in toluene (50 mL) in a Schlenk tube. Freshly distilled *N*,*N*-dimethyl-*p*-phenylenediamine (4 mmol, 545 mg) and a catalytic amount of *p*-toluenesulfonic acid were then added. The reaction mixture was heated to 85 °C and kept at this temperature for 8 h during which time the colour turned a deep-blue. The reaction mixture was cooled and the formed precipitate was filtered off and dried in vacuo; yield 546 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 2 H), 8.78 (d, 2 H), 8.70 (m, 4 H), 8.07 (d, 2

H), 7.91 (t, 2 H), 7.39 (t, 2 H), 7.26 (d, 4 H), 7.20 (d, 4 H), 3.07 (s, 12 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 188.3, 156.2, 156.1, 151.5, 149.2, 137.9, 136.9, 135.8, 129.0, 128.3, 125.6, 125.5, 125.3, 123.9, 121.4, 119.0, 112.25, 30.3 ppm. MS (DEI): *m/z* = 641 [M]$^+$. UV/Vis (THF): λ_{max} (lg ε) = 596 (4.16), 836 (4.05) nm. $C_{40}H_{35}N_9$ (641.74): calcd. C 74.86, H 5.50, N 19.64; found C 75.02, H 5.61, N 19.30.

Synthesis of Complex 1-Pd: In a 100 mL one-necked round-bottomed flask equipped with a magnetic stirrer was dissolved ligand **1** (1 mmol, 352 mg, Ar^1 = phenyl, Ar^2 = Ar^3 = 4-tolyl) in THF (35 mL). After addition of triethylamine (1 mmol, 0.14 mL) and a solution of Pd^{II} acetate (0.5 mmol, 112 mg) the reaction mixture was stirred at room temperature for 24 h. The resultant precipitate was filtered off and washed with THF. Afterwards, the precipitate was purified by chromatography on a short column (alumina, activity V, toluene/acetone, 12:1). The residue was extracted with methylene chloride and the resultant solution was evaporated to a small volume. The precipitated solid was filtered off, washed with *n*-pentane and dried in vacuo yielding the pure Pd complex; yield 120 mg (43%). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 8.17 (d, 4 H), 7.55 (t, 2 H), 7.40 (t, 4 H), 7.05 (d, 8 H), 6.76 (d, 8 H), 2.25 (s, 12 H) ppm. ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ = 199.3, 181.0, 140.1, 136.5, 134.1, 132.7, 130.4, 128.7, 128.2, 125.1, 20.9 ppm. MS (DEI): *m/z* = 807 [M – H]$^+$. UV/Vis (THF): λ_{max} (lg ε) = 630 (3.9) nm. $C_{46}H_{38}N_8Pd$ (809.24): calcd. C 68.27, H 4.73, N 13.85; found C 67.95, H 4.30, N 13.11.

Synthesis of Complex 1a-Pd: In a 100 mL one-necked round-bottom flask, equipped with a magnetic stirrer was dissolved ligand **1a** (1 mmol, 353 mg) in THF (60 mL). After addition of triethylamine (1 mmol, 0.14 mL) and a solution of (allyl)palladium(II) chloride dimer (1 mmol, 366 mg) in THF (20 mL), the reaction mixture was stirred at room temperature for 20 h. The resultant precipitate was filtered off and dried in vacuo yielding the pure Pd complex; yield 415 mg (64%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.18 (d, 1 H), 8.42 (d, 1 H), 8.16 (t, 1 H), 8.08 (m, 1 H), 7.38 (d, 4 H), 7.25 (d, 4 H), 5.75 (m, 1 H), 5.34 (m, 1 H), 3.99 (d, 1 H), 3.67 (m, 2 H, broad), 3.34 (m, broad, 3 H), 2.91 (d, 1 H), 2.74 (m, broad, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 190.4, 171.1, 155.5, 144.1, 139.7, 137.9, 129.6, 126.8, 124.8, 122.8, 121.9, 117.0, 109.7, 63.9, 61.7, 61.0, 21.2 ppm. MS (FAB in Nba): *m/z* = 648 [M + H]$^+$, 607 [M – allyl]$^+$, 500 [M – allyl – Pd]$^+$, 459 [M – 2 allyl – Pd]$^+$, 352 [M – H – 2 allyl-2 Pd]$^+$. UV/Vis (THF): λ_{max} (lg ε) = 557 (3.8), 590 (3.7) nm. $C_{28}H_{28}ClN_5Pd_2$ (682.83): calcd. C 49.25, H 4.13, N 10.26; found C 49.49.02, H 4.31, N 10.07.

Synthesis of Complex 1b-Pd: In a 100 mL one-necked round flask, equipped with a magnetic stirrer, **1b** (1 mmol, 584 mg) was dissolved in THF (50 mL). Triethylamine (1 mmol, 0.14 mL) and (allyl)palladium(II) chloride dimer (0.5 mmol, 183 mg) dissolved in THF (10 mL) were added dropwise at room temperature. The reaction mixture was heated to reflux for 2 h until completion. The mixture was evaporated to dryness and the remaining residue was suspended in methanol. The filtrate was again evaporated to dryness and purified by column chromatography (alumina, activity V, first toluene/ethyl acetate, 1:1, then pure THF). Although the homobimetallic complex is the main product, complex **1b-Pd** could be purified and isolated as a by-product by column chromatography since it is the only neutral complex formed in this reaction; yield 37 mg (5%). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 8.84 (s, 2 H), 8.74 (m, 4 H), 8.52 (d, 2 H), 8.01 (d, 2 H), 7.94 (t, 2 H), 7.60 (d, 4 H), 7.41 (t, 2 H), 7.26 (d, 4 H), 5.67 (m, 1 H), 3.67 (d, ^2J = 6.8 Hz, 2 H), 3.20 (d, ^2J = 12.4 Hz, 2 H), 2.43 (s, 6 H) ppm. ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ = 196.0, 177.8, 156.2, 156.0, 151.5, 149.2, 148.5, 143.5, 140.4, 136.8, 130.8, 128.9, 128.3, 127.0, 124.8, 123.8, 121.1, 118.7, 115.3, 61.7, 20.8 ppm. MS (FAB in Nba): *m/z* = 730 [M]$^+$, 689 [M – allyl]$^+$, 584 [M – allyl – Pd]$^+$.

Synthesis of Complex 1b-Ir: In a 100 mL one-necked round-flask, equipped with a magnetic stirrer, **1b** (0.5 mmol, 292 mg) and bis(2-phenylpyridine)iridium(I) chloride dimer (0.25 mmol, 268 mg) were suspended in DMF (50 mL). After addition of triethylamine (0.5 mmol, 0.07 mL) the reaction mixture was heated to 115 °C and kept on this temperature for 7 h. The resultant deep red solution was cooled and, after addition of water, the brown precipitate was filtered off, washed with water, diethyl ether, *n*-pentane and dried in vacuo; yield 412 mg (76%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.76 (m, 6 H), 8.51 (d, 2 H), 8.05 (d, 1 H), 7.94 (d, 2 H), 7.87 (t, 2 H), 7.72 (d+d, 2H+ 2 H, isochronic signals), 7.35 (m, 4 H), 7.14 (t, 2 H), 6.88 (d, 4 H), 6.72 (m, 8 H), 6.20 (d, 2 H), 2.17 (s, 6 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.6, 178.9, 168.4, 156.3, 156.0, 150.6, 149.2, 143.4, 143.0, 136.9, 136.7, 134.7, 134.6, 131.8, 130.8, 130.7, 129.6, 128.1, 126.8, 126.5, 125.0, 123.8, 122.3, 121.4, 121.1, 119.0, 118.5, 118.4, 117.3, 21.0 ppm. MS (FAB in Nba): *m/z* = 1085 [M + 2]$^+$. UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 518 (3.9), 625 (3.6) nm.

Crystal Structure Determination: The intensity data for the compound were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarisation effects but not for absorption effects.[19,20] The structure was solved by direct methods (SHELXS[21]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[22]). All hydrogen atoms were included in calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[22] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 1b-Ir:[23] $C_{60}H_{44}IrN_9{\cdot}2.5CHCl_3{\cdot}2H_2O$, *M* = 1453.73 g mol^{-1}, brown prism, size 0.06 × 0.06 × 0.02 mm, triclinic, space group $P\bar{1}$, *a* = 13.4240(9), *b* = 13.4260(8), *c* = 18.4943(13) Å, α = 82.233(4), β = 82.453(4), γ = 83.768(3)°, *V* = 3260.0(4) Å^3, *T* = –90 °C, *Z* = 2, $\rho_{calcd.}$ = 1.481 g cm^{-3}, μ(Mo-K_α) = 24.08 cm^{-1}, *F*(000) = 1458, 21717 reflections in *h*(–17/17), *k*(–17/16), *l*(–23/23), measured in the range $1.79° \leq \theta \leq 27.52°$, completeness θ_{max} = 96%, 14423 independent reflections, R_{int} = 0.067, 8165 reflections with $F_o > 4\sigma(F_o)$, 771 parameters, 0 restraints, R_{1obs} = 0.0876, wR_{2obs} = 0.2000, R_{1all} = 0.1731, wR_{2all} = 0.2418, GOOF = 1.035, largest difference peak and hole: 2.610/–0.943 e·Å^{-3}.

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[23] CCDC-719100 (for **1b-Ir**) contains 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.

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