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Synthesis, Structures and Comparison of Neutral Complexes Formed by 2-(2′-Pyridyl)indole and d^6 Transition Metals

Bernd Neumann,[a] Christoph Krinninger,[a] and Ingo-Peter Lorenz*[a]

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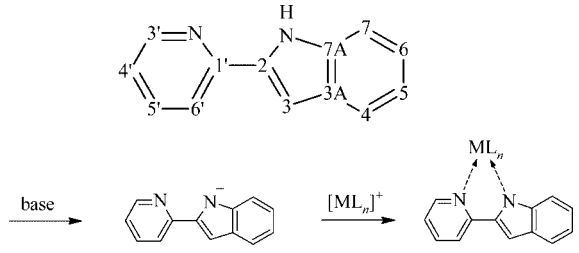
2-(2′-Pyridyl)indole acts as an N,N-bidentate ligand when deprotonated and forms (1-amido-4-imine)metallacycles with Re^{I}, Ru^{II}, Rh^{III} and Ir^{III}. The crystal structures of 2-(2′-pyridyl)indole and the complexes $[Re(C_{13}H_9N_2)(CO)_2(PPh_3)_2]$, $[Ru(C_{13}H_9N_2)(\eta^6\text{-}C_6Me_6)Cl]$, $[Rh(C_{13}H_9N_2)(\eta^5\text{-}C_5Me_5)Cl]$ and $[Ir(C_{13}H_9N_2)(\eta^5\text{-}C_5Me_5)Cl]$ are presented and their spectra discussed. This provides a foundation for the increased use of this ligand, which is a prototype of a monoanionic, bidentate N,N-chelating ligand. The introduction of negatively charged N,N-bidentate ligands can increase the possibility of synthesising complexes tailored to catalysis and other applications.

Introduction

Chelating ligands play an important role both in classical coordination chemistry and in modern organometallic chemistry. Both symmetrical and asymmetrical chelates with the same type of donor atoms or asymmetrical ones with different donor atoms have been reported, and the formation of five-membered metallacycles has been found to be preferred due to the increased stability of the resulting complexes. A 1,4-relationship of the donor atoms allows complexation of a broad range of metal ions in tetrahedral, octahedral and square-planar geometries. This can be achieved by minor changes in the ligand's geometry. Asymmetric chelation with two identical donor atoms occurs in two different types. First, the backbone bridge of the chelating ligand can induce asymmetry, as is observed with the axially chiral BINAP and related ligands.[1] Second, the two donor atoms can be electronically different, with one being assigned a negative charge or coordinating with sp^2 or sp^3 free electron pairs. Among the N,N-bidentate ligands, two types of symmetrical ligands have found widespread use, namely neutral diamine ligands such as ethylenediamine (en) and neutral diimine ligands like bipyridine (bpy) or 1,10-phenanthroline (phen). However, nonsymmetric anionic bidentate ligands have so far been much less investigated even though ligands of this type should be useful for several reasons. Firstly, they can be used to adjust the overall charge of the complex, which allows high formal oxidation states of the central atom to remain stable within such complexes. Secondly, they may facilitate proton channelling in or out of the complex centre, with the overall complex remaining mostly intact. Most catalytic cycles known in homogeneous catalysis involve the formation and modification of metal hydrides and protons. Both substrate movement towards and away from the complex as isomerisation occurs within a catalytic cycle will be affected by a proton acceptor. Thirdly, a bidentate ligand allows the former process to take place without cleavage of the ligand from the complex as an anionic ligand is more likely to tolerate an intermediate protonated stage than a neutral ligand. We selected 2-(2′-pyridyl)indole (Hpyind) as the first ligand to be examined within a series of noble metal complexes. After deprotonation, Hpyind is capable of acting as a 1,4-chelate, with one of the nitrogen donor atoms being an imine and the other being an amido function (Scheme 1). Further N,N- and N,P-chelating ligands will be presented and discussed in future publications.



Scheme 1. General numbering (except crystal structures) and reaction scheme.

Hpyind is a well-known molecule that has been investigated in several recent publications. Indeed, complexes with pyind-like structures included in a larger molecule were described[2,3] even before the first detailed study on the behav-

[a] Ludwig Maximilian University Munich, Department of Chemistry and Biochemistry,
Butenandtstr. 5–13, 81377 Munich, Germany
Fax: +49-89-2180-77867
E-mail: ipl@cup.uni-muenchen.de
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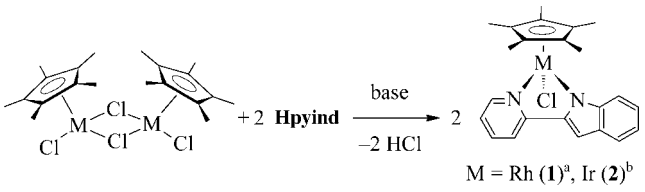
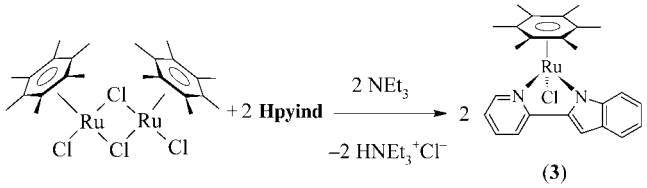
iour of Hpyind itself as a ligand was presented by Thummel et al.[4] Since the first isolated and structurally characterised pyind complex[5] with Rh^I was described, some other related complexes have been reported.[6–9] Recent work has concerned not only pyind complexes as catalysts in hydroarylation[10] and the Heck reaction,[11] but also its use in optical devices.[12–16] It has also been used in an organometallic mimic for the protein kinase staurosporin.[17–21] The authors of the latter complex pointed out the "solely structural role" of an inert ruthenium complex in the biological activity of this pyind derivative, and they achieved enhanced activity and selectivity of the biologically active centre by modifying the distant ruthenium's ligand sphere. The promising idea of using such inert complexes within organic molecules is new[21] and supports the application of specially tailored chelate ligands such as Hpyind. In detail, such an anionic pyind-type ligand can form stable complexes with highly charged central atoms better than similar neutral ligands. It also leaves more space for varying the coligands at the metal centre than most neutral and anionic polydentate ligands and can easily be modified at several positions. We have therefore investigated the reactivity of rhenium(I), ruthenium(II), rhodium(III) and iridium(III) precursor complexes towards Hpyind in the presence of an appropriate base.

Results and Discussion

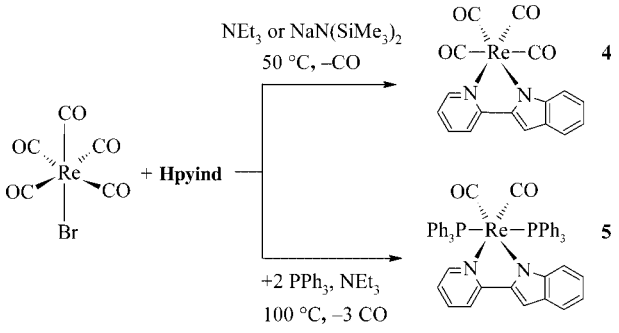
In the synthesis of the complexes reported here, we first use a strong amide base or potassium hydride for the deprotonation of Hpyind in a nonprotic solvent to which we then add the precursor complex. The synthetic strategy shown in Scheme 2 for the rhodium complex **1** works well, although the stoichiometry of the amide has to be strictly controlled as some side-reactions may occur when excess base is present. We further established that even weak bases such as triethylamine are capable of quantitatively abstracting the proton of Hpyind when it is acidified by pre-coordination of the precursor complex to the pyridine ring (Scheme 3). The resulting triethylammonium halide is easily precipitated from toluene or separated from the product by extraction into a small amount of ethanol. Only one product was obtained in the reactions of Ru^{II}, Rh^{III} and Ir^{III}, whereas the Re^I complex **5** required purification by flash chromatography in a dry and oxygen-free environment. We were unable to obtain an analytically pure sample of complex **4** from the reaction of $[Re(CO)_5Br]$ with Hpyind and $NaN(SiMe_3)_2$ or NEt_3. The result of this reaction is summarised in Scheme 4. Complex **4**, which contains an $Re(CO)_4$ moiety, is likely to be less stable than **5**, which is stabilised by the bulky axial PPh_3 groups. The IR spectrum of **4** supports a pseudo-C_{2v} symmetry and shows four ν(C=O) absorptions at 2015, 1936, 1912 and 1891 cm^{-1}. Upon evaporation of toluene, or in a more polar solvent like acetone, only two frequencies are observed [2011 and 1892 cm^{-1} (br.)], thus suggesting a *fac*-$Re(CO)_3$ species. The DEI mass spectrum shows only an $[Re(CO)_3(pyind)]^+$ fragment as the highest peak.



Scheme 2. Formation of rhodium and iridium complexes **1** and **2**; [a] toluene, $NaN(SiMe_3)_2$, 60 °C; [b] CH_2Cl_2, NEt_3, 25 °C.



Scheme 3. Synthesis of ruthenium complex **3**.



Scheme 4. Formation of complexes **4** and **5**.

The isolated complexes **1**–**3** are stable under argon at room temperature. However, some decomposition can be observed in moist air after several days. Solutions of these complexes in dichloromethane are stable for days, whereas the addition of methanol or moisture leads to the appearance of several new signals in the NMR spectra and decomposition. Complex **5** is somewhat more sensitive, and its decomposition is indicated by the formation of an intense green colour after a few seconds when the complex is exposed to moist air. All of the complexes show a high thermal stability, which makes them suitable for direct mass spectrometry.

The ^1H NMR spectrum of Hpyind has been described in the literature[4] but we have found some minor errors in the previous assignment concerning $H^{3'}$, $H^{4'}$, H^4 and $H^{6'}$. We therefore conducted H,H-COSY and HMQC measurements for both Hpyind and complex **1** in order to better understand the effect of complexation. These 2D NMR spectra of Hpyind and **1** are given as Supporting Information. Upon complexation, the NH signal of Hpyind disappears completely, the signals of H^5 and H^6 are shifted upfield by about 0.2 ppm, while those of $H^{5'}$, $H^{6'}$ and H^7 remain largely unaffected in complexes **1**–**3**. The signal of H^3 is affected only in the iridium complex **2**, where it is

shifted upfield by 0.1 ppm. Complex **5** shows a different picture due to the lower metal oxidation state, because the phosphane ligands are more electron-donating and the protons of pyind are affected by the phenyl groups of PPh_3 (ring current). The signals of the pyridine ring protons are shifted upfield by about 1.1 ppm on average, thereby indicating a highly electron-enriched aromatic system. All complexes give nearly identical peaks for the C–H carbon atoms in the ^{13}C NMR spectra, with C^7, which shows a 5 ppm downfield shift, being the only significantly shifted signal. The four quaternary carbon signals are shifted downfield, by about 7 ppm for $C^{1'}$, about 10 ppm for C^2 and C^{7A} and about 3 ppm for C^{3A}, in all complexes. This effect is well known for metallacycle carbon atoms but somewhat surprising for the other ones. To conclude, the main effect of complexation is observed at the benzene ring of the indole moiety, and no major change is expected in the pyridylpyrrole moiety.

The mass spectra show no unexpected behaviour and are easily interpreted as a result of the metal and halide isotope distribution. The main fragmentation pattern is given by splitting off the ligands one after another.

The IR spectra of the complexes show a common strong band at around 1610 cm^{-1} for ν(C=N) and lack the indole ν(NH) band of Hpyind at 3450 cm^{-1}. The two carbonyl bands of complex **5** indicate the sole presence of the *cis* conformation in solution, as was also observed in the crystal structure of **5**. They appear at very low energy ($\tilde{\nu}$ = 1905, 1823 cm^{-1}), in the range of terminal carbonyl ligands. Similar low frequencies have been reported for anionic complex radicals of rhenium(I).[22]

The electronic spectra of Hpyind have been discussed previously.[23–25] On complexation, the absorption maximum at 325 nm in Hpyind[4] shows a bathochromic shift of 40–65 nm. Table 1 shows this effect to be affected by the metal's charge and that it is stronger for complexes containing fifth-row metals than those with fourth-row metals.

Table 1. UV absorption data for pyind complexes in CH_2Cl_2.

	λ_{max} [nm] (ε [M^{-1} cm^{-1}])	λ_{max} [nm] (ε [M^{-1} cm^{-1}])	λ_{max} [nm] (ε [M^{-1} cm^{-1}])
1	363 (15890)	314 (9000)	260 (16680)
2	377 (14620)	326 (10800)	260 (15240)
3	374 (11670)	331 (9860)	248 (14760)
5	367 (11335)	323 (11430)	

As several structure-related questions about Hpyind have been discussed in the literature, we were surprised to find that the crystal structure was unknown. In these studies, bridging methylene chains have been attached to restrain the nitrogen atoms in a *cis* conformation,[4] and tautomeric forms upon *N*-methylation have been studied.[26] After recrystallisation from chloroform/hexane we obtained colourless single crystals of Hpyind. An ORTEP plot of the molecular structure is displayed in Figure 1, which shows that Hpyind exists in a *cis* conformation in the solid state. The indole and pyridyl moieties are somewhat twisted by about 14°, as shown by the dihedral angle N(1)–C(1)–C(9)–N(2) given in Table 2. Within the crystal, two Hpyind molecules form a dimeric unit where the planes of the two Hpyind molecules form an angle of 110.8°. They are connected by two hydrogen bonds, where H(1) is refined freely between N(1) of one molecule and N(2) of the other molecule with an almost ideal N(1)–H(1)–N(2) angle of 170(2)° and an N(1)–N(2) distance of 2.988(3) Å, which indicates a strong interaction. The luminescent beryllium complex of pyind reported by Liu et al.[16] shows a similar structure. In order to compare the changes in the pyind moiety on complexation, some interatomic distances have been summarised in Table 3. In all our complexes the pyind ligand becomes planar, with the previously mentioned dihedral angle reduced to almost zero. This is accompanied by a significant shortening of the C(1)–C(9) bond. Together with these two carbon atoms, the two nitrogen donor atoms and

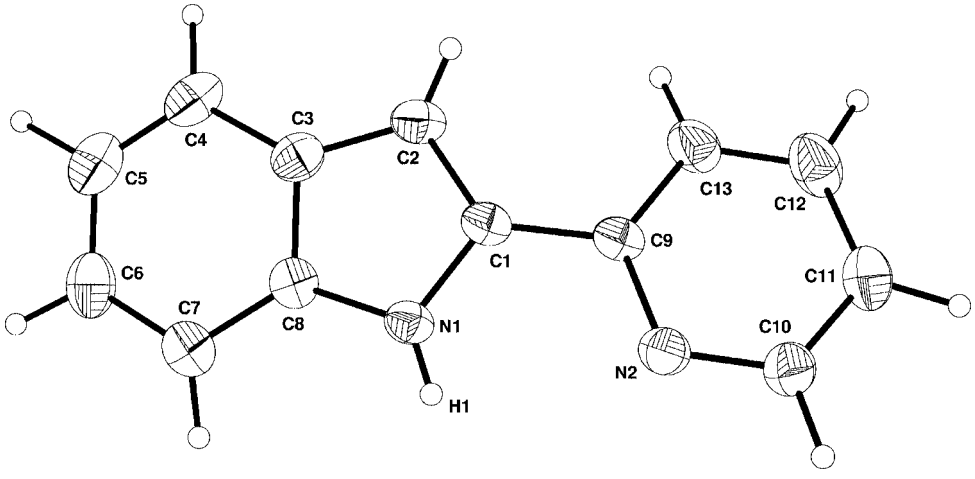


Figure 1. ORTEP plot (25% probability) of Hpyind. The numbering displayed is used in the discussion of all crystal structures for the pyind moiety.

Table 2. Selected angles [°] and dihedral angles [°].

	Hpyind	1	2	3	5
Cl(1)–M(1)–N(1)		88.55(6)	86.69(10)	87.72(9)	
Cl(1)–M(1)–N(2)		87.45(5)	85.62(10)	88.70(9)	
N(1)–M(1)–N(2)		76.79(8)	76.12(14)	76.08(12)	74.73(9)
M(1)–N(1)–C(1)		116.6(3)	116.07(16)	114.3(3)	116.20(19)
M(1)–N(2)–C(9)		117.1(3)	115.47(16)	115.3(3)	116.49(19)
N(1)–C(1)–C(9)	121.28(17)	115.9(2)	115.4(4)	114.9(3)	117.6(2)
N(2)–C(9)–C(1)	117.18(17)	115.0(2)	114.1(4)	113.8(3)	114.9(2)
N(1)–C(1)–C(9)–N(2)	–13.8(3)	–3.7(3)	3.3(5)	–4.1(5)	–2.0(4)

the metal atom form a coplanar five-membered metallacycle. The pyind ligand has quite a small bite angle of 74–77°, which makes it a nonideal ligand for large atoms. As it fits well into the octahedral coordination geometry of d^6 complexes, this deficiency seems to be compensated for by its charge transfer to the metal centre.

Table 3. Selected interatomic distances [Å].

	Hpyind	1	2	3	5
M(1)–N(1)		2.073(2)	2.050(3)	2.082(3)	2.153(2)
M(1)–N(2)		2.1343(19)	2.103(3)	2.108(3)	2.202(2)
M(1)–Cl(1)		2.3987(8)	2.3860(12)	2.4142(10)	
N(1)–C(1)	1.372(3)	1.375(3)	1.378(5)	1.382(4)	1.382(4)
C(1)–C(9)	1.458(3)	1.440(4)	1.421(6)	1.446(6)	1.427(4)
C(9)–N(2)	1.342(3)	1.355(3)	1.342(5)	1.366(5)	1.368(4)

The Rh^{III} complex **1** (Figure 2) and the Ir^{III} complex **2** (Figure 3) are very similar, as would be expected, but some differences should be emphasised. The C(9)–N(2) distance increases in all complexes relative to the noncoordinated Hpyind ligand, but it remains unchanged in complex **2**. This is in agreement with the shorter metal–ligand contacts and the shorter C(1)–C(9) distance observed. As the Rh^{III} centre in complex **1** should be smaller than Ru^{II} in complex **3** (Figure 4), the latter would be expected to show larger metal–ligand distances. This is true for the slightly larger N(1)–Ru(1) distance, although the N(2)–Ru(1) distance is shortened by 0.05 Å. On the contrary, the shorter distances in complex **2** along with the shorter distances in the metallacycle mean that the ruthenium metallacycle of **3** has larger intraligand distances than found in **1**.

When complex **5** (Figure 5) is considered, the different co-ligand situation in this complex compared to the other complexes has to be taken in account. The two axial phosphane ligands show virtually identical Re–P distances of

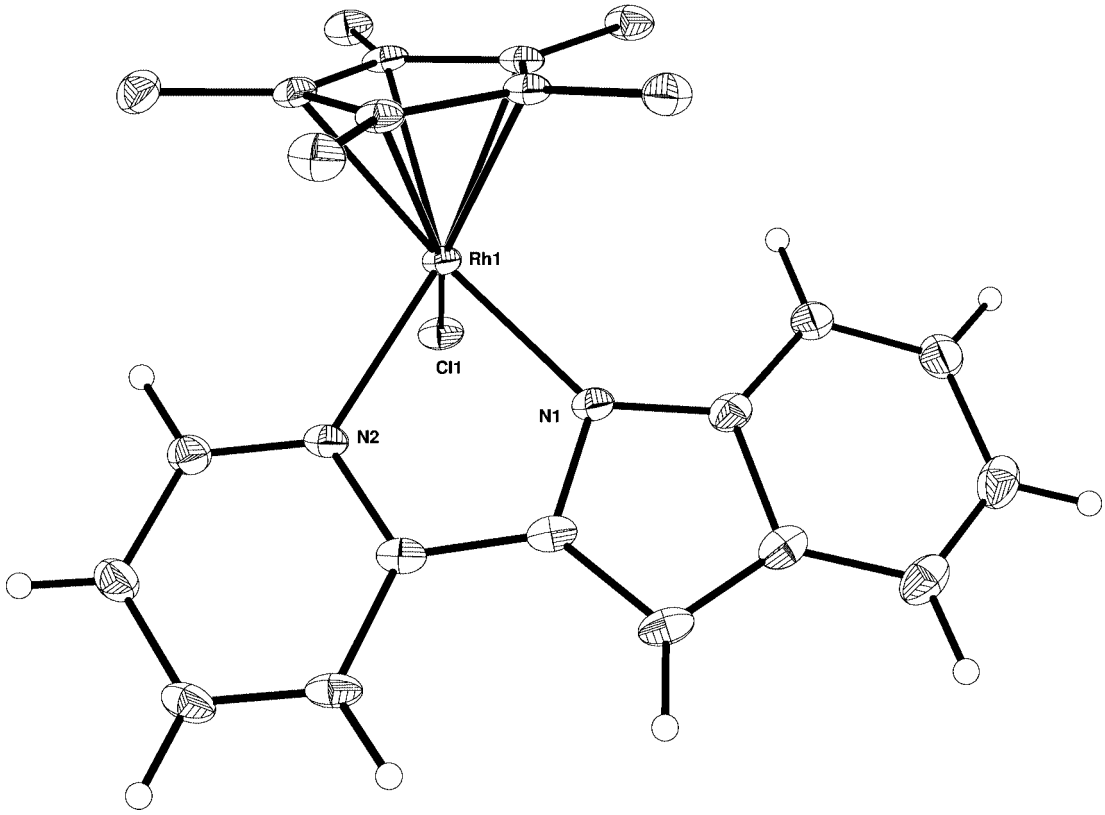


Figure 2. Molecular structure of rhodium complex **1** (25% probability). The methyl protons of C_5Me_5 are omitted for clarity.

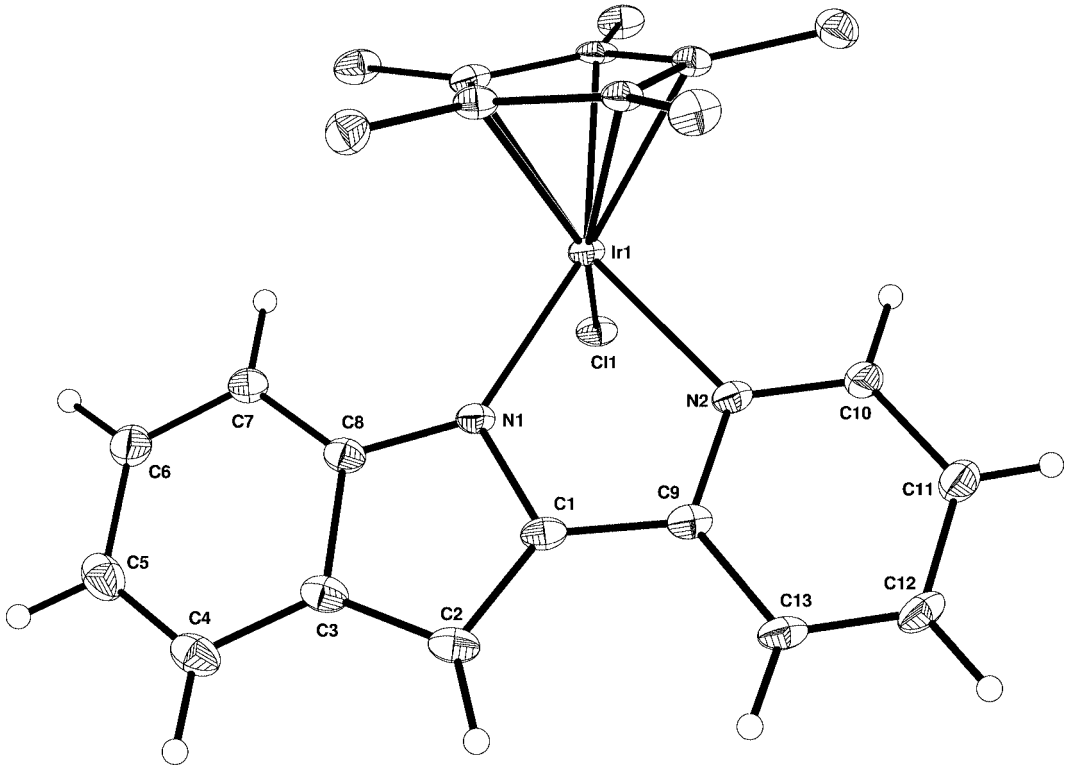


Figure 3. Molecular structure of complex **2** (25% probability). The methyl protons of C_5Me_5 are omitted.

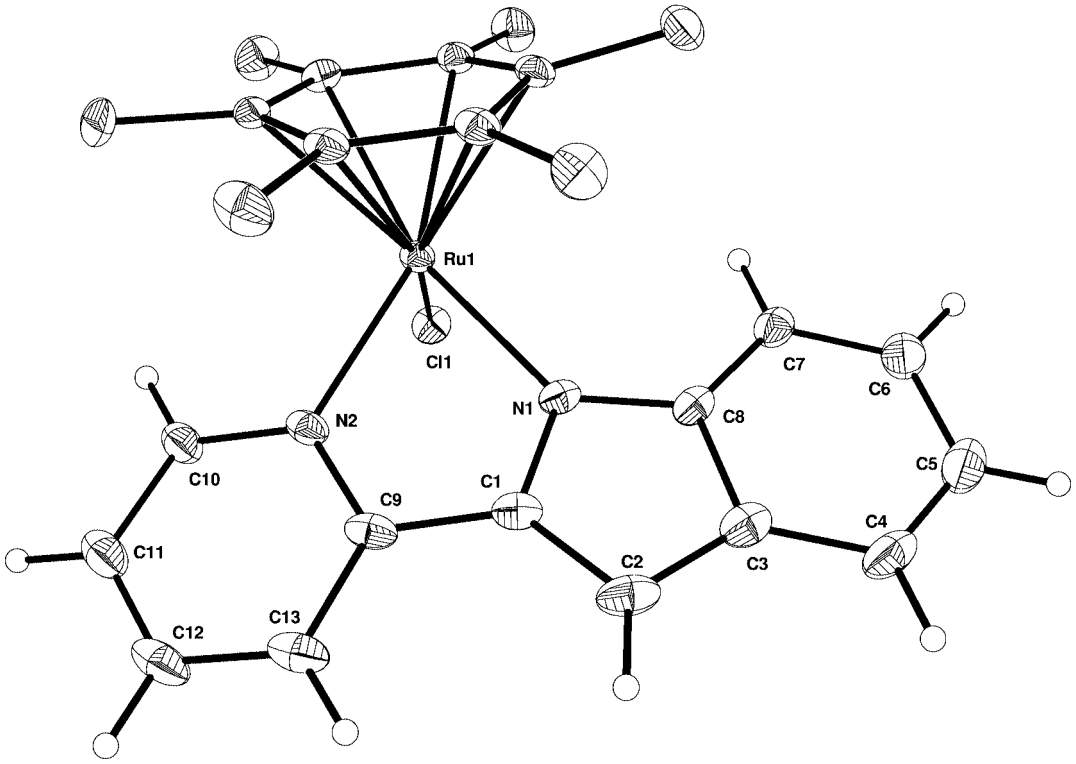


Figure 4. ORTEP plot of complex **3** (25% probability). The 18 disordered protons of the hexamethylbenzene moiety are omitted and a solvent molecule of CH_2Cl_2 is not included in the diagram.

2.4273(9) and 2.4324(9) Å, respectively, and all of the P–C distances of the phenyl groups lie between 1.832(3) and 1.837(3) Å. Two linear carbonyl ligands, which can act as both σ-donors and π-acceptors, are found in the *trans* positions with respect to the nitrogen donors. The very low C=O valence vibration energy observed suggests these car-

bonyl groups absorb a considerable amount of electron density. The low-valent rhenium(I) centre is larger than the optimum size for a chelating pyind ligand. Both of the Re–N distances are 0.10 Å longer than in the iridium complex **2**. However, the ligand shows both a shortened C(1)–C(9) bond, as was observed in compound **2**, as well as longer C=N bonds, as in **3**.

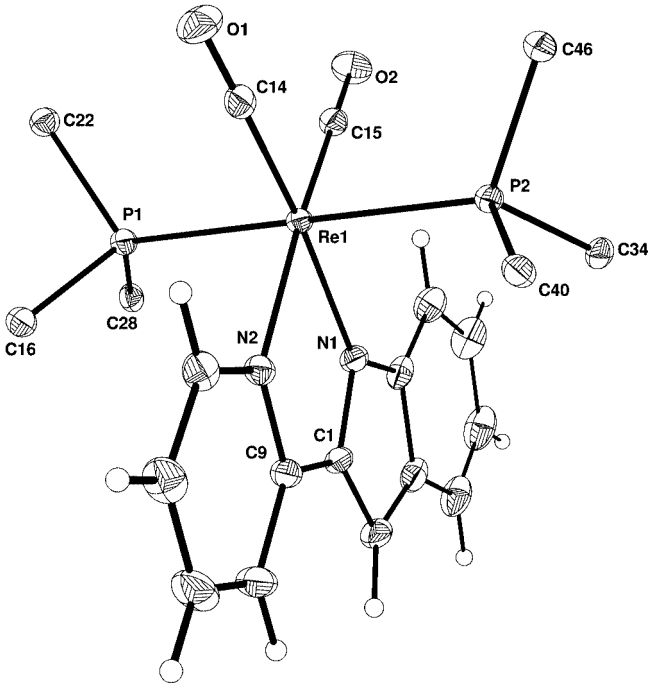


Figure 5. ORTEP plot of the rhenium compound **5** (25% probability). Only the terminal carbon atoms of both axial triphenylphosphane ligands are displayed. One disordered molecule of toluene is omitted.

Conclusion

We have synthesised a series of novel transition metal complexes with the bidentate amido–imine ligand 2-(2′-pyridyl)indole. This is the first study to compare the properties that arise when different central atoms are used to form amido–imine complexes. Work on related anionic bidentate ligands, such as further modified amido–imine ligands and amido–phosphane ligands, is currently in progress. In addition, complexes containing different oxidation states for the central atoms, especially d^8 systems such as Rh^{I}, Ir^{I} and Pd^{II}, will also be investigated. Investigations into the catalytic activity and optimisation of these complexes to improve certain catalytic processes are also underway.

Experimental Section

General: All reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents were purified by standard procedures; dichloromethane was distilled from calcium hydride. The complexes $[RhCl_2Cp^*]_2$,[27] $[IrCl_2Cp^*]_2$,[27] $[Ru(CO)_2ClCp^*]$,[28] $[Ru(C_6Me_6)Cl_2]_2$[29] and $[Re(CO)_5Br]$[30] and Hpyind[4] were prepared and purified according to literature procedures. NMR spectra were measured with a Jeol Eclipse 270, Jeol Eclipse 400 or Jeol EX 400 spectrometer; the chemical shifts are given relative to external standards (TMS and 85% H_3PO_4). Mass spectra were recorded with a Jeol MStation JMS 700. IR spectra were recorded from KBr pellets or solutions in an NaCl cell using a Perkin–Elmer Spectrum One FT-IR spectrometer. UV/Vis spectra were measured in glass cuvettes with a Perkin–Elmer Lambda 16 spectrometer. The melting points, obtained with a Büchi 510 apparatus, are uncorrected. Elemental analysis was performed by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU, using a Hereaus Elementar Vario El apparatus.

2-(2′-Pyridyl)indol (Hpyind): This compound was prepared according to the procedure reported by Thummel[4] and recrystallised from chloroform/hexanes. The following NMR assignments differ slightly from the literature. The 2D NMR spectra are given as Supporting Information. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 9.79 (s, 1 H, NH), 8.57 (ddd, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.6, $^5J_{H,H}$ = 1.0 Hz, 1 H, H$^{3'}$), 7.82 (dt, $^3J_{H,H}$ = 8.0, $^{4,5}J_{H,H}$ = 1.0 Hz, H$^{6'}$), 7.73 (td, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.6 Hz, H$^{5'}$), 7.62 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.0 Hz, H^4), 7.38 (dd, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.0 Hz, H^7), 7.18 (td, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.0 Hz, 1 H, H^6), 7.18 (ddd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 5.2, $^4J_{H,H}$ = 1.0 Hz, H$^{4'}$), 7.08 (td, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ = 1.0 Hz, 1 H, H^5), 7.02 (dd, $^4J_{H,H}$ = 2.0, $^5J_{H,H}$ = 1.0 Hz, 1 H, H^3) ppm. ^{13}C NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 150.3 (C$^{1'}$), 149.2 (C$^{3'}$), 136.9 (C^2), 136.7 (C$^{5'}$), 136.6 (C^{7A}), 129.2 (C^{3A}), 123.1 (C^6), 122.1 (C$^{4'}$), 121.1 (C^4), 120.1 (C^5), 119.9 (C$^{6'}$), 111.4 (C^7), 100.3 (C^3) ppm.

Chlorido(η^5-pentamethylcyclopentadienido)[2-(2′-pyridyl)indolido-*N*,*N*′]rhodium(III) (1): A 1 M solution of $NaN(SiMe_3)_2$ (280 μL, 0.28 mmol) was added to a solution of Hpyind (54 mg, 0.28 mmol) in toluene (10 mL). The mixture was stirred for 15 min and a solution of $[Rh_2Cl_4Cp^*_2]$ (85 mg, 0.14 mmol) in toluene (20 mL) was added dropwise. The red solution became darker and was stirred at 60 °C; after 10 min, an orange precipitate had formed. After 60 min, precipitation was complete and complex **1** was filtered, washed with cold toluene and dried in vacuo (115 mg, 0.25 mmol, 89%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.54 (br. d, $^3J_{H,H}$ = 5.7 Hz, 1 H, H$^{3'}$), 7.76 (ddd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.7, $^4J_{H,H}$ = 0.8 Hz, 1 H, H$^{6'}$), 7.71 (ddd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 7.0, $^4J_{H,H}$ = 1.5 Hz, 1 H, H$^{5'}$), 7.57 (dt, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.1 Hz, 1 H, H^4), 7.39 (dq, $^3J_{H,H}$ = 8.2, $^{4,5}J_{H,H}$ = 1.0 Hz, 1 H, H^7), 7.14 (ddd, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1.7 Hz, 1 H, H$^{4'}$), 7.04 (ddd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.1 Hz, 1 H, H^6), 7.00 (d, $^4J_{H,Rh}$ = 1.1 Hz, 1 H, H^3), 6.88 (ddd, $^3J_{H,H}$ = 7.9, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.0 Hz, 1 H, H^5), 1.62 (s, 15 H, Cp*) ppm. ^{13}C NMR (100.52 MHz, CD_2Cl_2, 25 °C): δ = 157.4 (C$^{1'}$), 150.3 (C$^{3'}$), 145.8 (C^2), 144.9 (C^{7A}), 137.8 (C$^{5'}$), 132.5 (C^{3A}), 121.8 (C^4), 121.6 (C$^{4'}$), 120.9 (C^6), 119.8 (C$^{6'}$), 117.7 (C^5), 115.3 (C^7), 101.2 (C^3), 94.6 (d, $^1J_{C,Rh}$ = 7.7 Hz, Cp*), 9.4 (s, Cp*) ppm. DEI-MS (70 eV): *m*/*z* (%) = 466 (10) [M$^+$], 431 (100) [M$^+$ – Cl], 237 (17) [RhCp* – H], 235 (15) [RhCp* – 3 H], 194 (13) [pyind]. IR (KBr) $\tilde{\nu}$ = 3047 (w), 2984 (w), 2914 (w), 1607 (s), 1536 (s), 1449 (s), 1350 (m), 1310 (m), 1271 (w), 1199 (w), 1156 (m), 1119 (w), 1019 (m), 763 (s), 753 (m) cm^{-1}; (CH_2Cl_2) $\tilde{\nu}$ = 3049 (m), 2978 (w), 2918 (w), 1608 (s), 1537 (s), 1453 (s), 1361 (m), 1350 (m), 1312 (m), 1262 (m), 1200 (w), 1154 (m), 1141 (w), 1118 (w), 1077 (w), 1023 (m), 963 (w) cm^{-1}. UV/Vis (CH_2Cl_2, 25 °C): λ (ε) = 363 (15890), 314 (9000), 260 (16680 M^{-1} cm^{-1}) nm. $C_{23}H_{24}ClN_2Rh$ (466.81): calcd. C 59.18, H 5.18, N 6.00; found C 58.57, H 5.24, N 5.88. M.p. 305 °C (dec.). Single crystals suitable for X-ray structure determination were obtained by diffusion of pentane into a solution of **1** in CH_2Cl_2.

Chlorido(η^5-pentamethylcyclopentadienido)[2-(2′-pyridyl)indolido-*N*,*N*′]iridium(III) (2): Hpyind (59 mg, 0.3 mmol) and [$Ir_2Cl_4Cp^*_2$] (120 mg, 0.15 mmol) were dissolved in CH_2Cl_2 (5 mL) and NEt_3 (42 μL, 0.4 mmol) was added. After stirring at room temp. for 48 h, the solvent was evaporated. The yellow residue was stirred with EtOH (3 × 5 mL) to remove $HNEt_3Cl$ and the slightly yellow solution was discarded after centrifugation. Drying in vacuo yielded **2** (135 mg, 0.24 mmol, 81%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.55 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, H$^{3'}$), 7.81 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, H$^{6'}$), 7.70 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H, H$^{5'}$), 7.54 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, H^4), 7.37 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, H^7), 7.09 (dd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 5.8 Hz, 1 H, H$^{4'}$), 7.01 (dd, $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.8 Hz, 1 H, H^6), 6.91 (s, 1 H, H^3), 6.90 (dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 6.8 Hz, 1 H, H^5), 1.66 (s, 15 H, Cp*) ppm. ^{13}C NMR (100.52 MHz, CD_2Cl_2, 25 °C): δ = 158.1 (C$^{1'}$), 150.4 (C$^{3'}$), 145.3 (C^2), 144.9 (C^{7A}), 138.1 (C$^{5'}$), 131.5 (C^{3A}), 122.1 (*C*^{4} and C$^{4'}$), 121.7 (C^6), 119.6 (C$^{6'}$), 118.1 (C^5), 115.2 (C^7), 101.8 (C^3), 86.8 (Cp*), 9.6 (Cp*) ppm. DEI-MS: *m*/*z* (%) = 556 (65) [M$^+$], 521 (100) [M$^+$ – Cl], 363 (20) [IrCp*Cl], 323 (17) [Ir(C$_7$H$_{11}$)Cl]. IR (KBr) $\tilde{\nu}$ = 3052 (w), 2986 (w), 1609 (s), 1541 (s), 1491 (w), 1447 (s), 1371 (w), 1349 (m), 1311 (m), 1266 (w), 1203 (w), 1155 (m), 1122 (m), 1082 (w), 1022 (m), 965 (w), 769 (s), 753 (s), 517 (w), 443 (w), 376 (w) cm^{-1}; (CH_2Cl_2) $\tilde{\nu}$ = 3047 (w), 2978 (w), 2921 (w), 1612 (s), 1453 (s), 1450 (s), 1381 (w), 1360 (w), 1359 (m), 1314 (m), 1202 (w), 1155 (w), 1120 (w), 1080 (w), 1030 (m) cm^{-1}. UV/Vis (CH_2Cl_2, 25 °C): λ (ε) = 377 (14620), 326 (10800), 260 (15240), 226 (24740 M^{-1} cm^{-1}) nm. $C_{23}H_{24}ClIrN_2$ (556.12): calcd. C 49.67, H 4.35, N 5.04; found C 49.43, H 4.15, N 4.90. M.p. 305–307 °C (dec.). Single crystals suitable for X-ray structure analysis were obtained by diffusion of pentane into a solution of **2** in CH_2Cl_2.

Chlorido(hexamethylbenzene)[2-(2′-pyridyl)indolido-*N*,*N*′]-ruthenium(II) (3): Hpyind (78 mg, 0.4 mmol) and [$Ru_2Cl_4(C_6Me_6)_2$] (134 mg, 0.2 mmol) were dissolved in CH_2Cl_2 (10 mL) and NEt_3 (30 μL, 0.4 mmol) was added. After stirring at room temp. for 24 h, the NMR spectrum indicated quantitative reaction. The solution was concentrated in vacuo and the residue was stirred with a small amount of EtOH (2 × 3 mL) to remove $HNEt_3Cl$. The EtOH solution was discarded after centrifugation from the insoluble residue, which was dried to give **3** as a yellow to orange powder (153 mg, 0.31 mmol, 78%). ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C): δ = 8.49 (ddd, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 1.4, $^5J_{H,H}$ = 1.0 Hz, 1 H, H$^{3'}$), 7.65 (ddd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.4, $^5J_{H,H}$ = 1.0 Hz, 1 H, H$^{6'}$), 7.62 (ddd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 6.5, $^4J_{H,H}$ = 1.4 Hz, 1 H, H$^{5'}$), 7.53 (dt, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.0 Hz, 1 H, H^4), 7.30 (dq, $^3J_{H,H}$ = 8.4, $^{4,5}J_{H,H}$ = 1.0 Hz, 1 H, H^7), 7.06 (td, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, H$^{4'}$), 7.00 (ddd, $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.4 Hz, 1 H, H^6), 6.94 (d, $^4J_{H,H}$ = 0.8 Hz 1 H, H^3), 6.87 (ddd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.1 Hz, 1 H, H^5), 1.98 (s, 18 H, C$_6$Me$_6$) ppm. ^{13}C NMR (67.9 MHz, CD_2Cl_2, 25 °C): δ = 157.5 (C$^{1'}$), 151.9 (C$^{3'}$), 146.6 (C^2), 144.3 (C^{7A}), 137.0 (C$^{5'}$), 132.3 (C^{3A}), 121.6 (C^4), 120.7 (C$^{4'}$), 120.1 (C^6), 118.9 (C$^{6'}$), 117.6 (C^5), 116.0 (C^7), 101.2 (C^3), 93.1 (C$_6$Me$_6$), 15.8 (C$_6$Me$_6$) ppm. FAB-MS: *m*/*z* (%) = 493 (25) [MH$^+$], 492 (28) [M$^+$], 457 (100) [M$^+$ – Cl]. IR (KBr) $\tilde{\nu}$ = 3039 (w), 1605 (s), 1532 (s), 1446 (s), 1383 (w), 1360 (w), 1347 (m), 1309 (s), 1261 (m), 1226 (w), 1150 (w), 1115 (w), 1071 (m), 1036 (m), 1020 (m), 782 (m), 769 (m), 748 (m), 517 (w), 456 (w), 373 (w) cm^{-1}; (CH_2Cl_2) $\tilde{\nu}$ = 3052 (m), 2977 (w), 2923 (w), 1608 (s), 1534 (s), 1447 (s), 1386 (w), 1361 (w), 1348 (m), 1312 (m), 1199 (w), 1153 (w), 1118 (w), 1075 (w), 1021 (m), 960 (w), 895 (w) cm^{-1}. UV/Vis (CH_2Cl_2, 25 °C): λ (ε) = 374 (11670), 331 (9860), 248 (14760), 229 (20135 M^{-1} cm^{-1}) nm. $C_{25}H_{27}ClN_2Ru$ (492.02): calcd. C 61.03, H 5.53, N 5.69; found C 58.30, H 5.58, N 5.34. M.p. >320 °C. Single crystals suitable for X-ray structure analysis were obtained by diffusion of pentane into a solution of **3** in CH_2Cl_2. They contain one molecule of CH_2Cl_2 per formula unit.

Tetracarbonyl[2-(2′-pyridyl)indolido-*N*,*N*′]rhenium(I) (4): Hpyind (97 mg, 0.5 mmol) was dissolved in toluene (10 mL) and a solution of [$Re(CO)_5Cl$] (181 mg, 0.5 mmol) in toluene (10 mL) was added. A 0.1 M solution of $NaN(SiMe_3)_2$ in toluene (5.0 mL) or NEt_3 (75 μL, 0.5 mmol) was then added and the mixture stirred at 50 °C. Concentration of the solution after 16 h yielded a blue-green solid that dissolved readily in acetone or CH_2Cl_2. All our attempts to crystallise the substance by diffusion of a non-polar solvent into a solution of **4** or by cooling were not successful. NMR signals in the aromatic region are broad and could not be unambiguously interpreted. DEI-MS (70 eV): *m*/*z* (%) = 464 (89) [M$^+$ – CO], 436 (50) [M$^+$ – 2 CO], 408 (53) [M$^+$ – 3 CO], 380 (100) [Re(pyind)], 353 (25) [Re(pyind) – HCN]. IR (toluene) $\tilde{\nu}$ = 2015 (vs), 1936 (m), 1912 (vs), 1891 (vs) cm^{-1}; (acetone) $\tilde{\nu}$ = 2011 (vs), 1892 (vs) cm^{-1}; (toluene, from NEt_3 run) $\tilde{\nu}$ = 2010 (vs), 1891 (vs) cm^{-1}. Further details of the characterisation are not available.

Dicarbonyl[2-(2′-pyridyl)indolido-*N*,*N*′]bis(triphenylphosphane)-rhenium(I) (5): Hpyind (39 mg, 0.2 mmol), [$Re(CO)_5Br$] (81 mg, 0.2 mmol), PPh_3 (106 mg, 0.4 mmol) and NEt_3 (31 μL, 0.22 mmol) were dissolved in toluene (5 mL) and stirred in a sealed Schlenk tube at 100 °C for 48 h. The hot yellow-brown solution was separated from the colourless precipitate ($HNEt_3Cl$). The IR spectrum shows several carbonyl bands, thereby indicating that a mixture of species is present. The solution was cooled to –32 °C overnight and a yellow precipitate formed. This was separated (80 mg, 42%) from the solution and purified using a short chromatography column [SiO_2 60, 70–230 mesh, 250 mL (!) CH_2Cl_2]. An air- and moisture-free environment must be maintained during the entire workup process as the crude product easily decomposes to form an intensely green oil, whereas the final pure product is considerably more stable. Drying yielded **5** as a yellow solid (70.2 mg, 73 μmol, 37%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.64–7.66 (m, 1 H, H^4), 7.46 (br. d, $^3J_{H,H}$ = 5.2 Hz, H$^{3'}$), 7.15 (dd, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, 1 H, H^7), 7.12 (ddd, $^3J_{H,H}$ = 8.0, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, H^6), 7.08–7.11 (m, 18 H, PPh_3), 6.99–7.01 (m, 12 H, PPh_3), 6.97–6.98 (m, 1 H, H^5), 6.85 (d, $^4J_{H,H}$ = 1.0 Hz, H^3), 6.63 (dd, $^3J_{H,H}$ = 6.0, $^3J_{H,H}$ = 5.2 Hz, 1 H, H$^{4'}$), 6.63 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, H$^{6'}$), 6.00 (ddd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 1.6 Hz, 1 H, H$^{5'}$) ppm. ^{13}C NMR (100.63 MHz, CD_2Cl_2, 25 °C): δ = 156.9 (C$^{1'}$), 151.6 (C$^{3'}$), 147.8 (C^2), 145.9 (C^{7A}), 135.3 (C$^{5'}$), 133.5 (t, $J_{C,P}$ = 5.3 Hz, PPh_3), 132.2 (C^{3A}), 129.1 (PPh_3), 127.7 (t, $J_{C,P}$ = 4.3 Hz, PPh_3), 120.49 (C^4), 120.47 (C$^{4'}$), 120.0 (C^6), 118.6 (C$^{6'}$), 117.8 (C^5), 117.1 (C^7), 101.4 (C^3) ppm. ^{31}P NMR (162.00 MHz, CD_2Cl_2, 25 °C): δ = 21.05 ppm. DEI-MS (70 eV): *m*/*z* (%) = 960 (7) [M$^+$], 698 (5) [M$^+$ – PPh_3], 642 (9) [Re(PPh_3)(pyind)], 262 (100) [PPh_3], 183 (45) [PPh_2]. IR (KBr) $\tilde{\nu}$ = 1905 (vs), 1823 (vs), 1609 (m), 1533 (m), 1481 (m), 1455 (w), 1444 (m), 1432 (s), 1367 (w), 1349 (w), 1318 (w), 1263 (w), 1153 (w), 1091 (m), 741 (s), 694 (s), 613 (w), 518 (s), 413 (w) cm^{-1}. UV/Vis (CH_2Cl_2, 25 °C) λ (ε) = 367 (11335), 323 (11430 M^{-1} cm^{-1}) nm. $C_{51}H_{39}N_2O_2P_2Re$ (960.02): calcd. C 63.81, H 4.09, N 2.92; found C 59.19, H 3.86, N 2.56. M.p. 211–214 °C (dec.). Single crystals suitable for X-ray structure determination were obtained from the initial toluene solution after separating the $HNEt_3Cl$ and cooling from 100 °C to room temp. within 10 h. The yellow, block-shaped crystals contain one molecule of toluene per formula unit.

X-ray Crystallography: X-ray crystallographic data (Table 4) were collected with a Nonius Kappa CCD and with an Oxford Diffraction Xcalibur S, both using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods with

Table 4. Crystallographic data of Hpyind as well as complexes **1**–**3** and **5**.

	Hpyind	**1**	**2**	**3**	**5**
Empirical formula	$C_{13}H_{10}N_2$	$C_{23}H_{24}ClN_2Rh$	$C_{23}H_{24}ClIrN_2$	$C_{26}H_{29}Cl_3N_2Ru$	$C_{58}H_{47}N_2O_2P_2Re$
Formula mass [amu]	194.232	466.808	556.120	576.95	1052.161
Temperature [K]	200(2)	200(2)	200(2)	200(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P4_12_12$	$P2_1/n$	$P2_1/n$	*Pbca*	$P2_1/c$
a [Å]	8.4513(12)	8.2365(16)	8.2178(16)	8.5237(17)	12.278(3)
b [Å]	8.4513(12)	14.495(3)	14.302(3)	19.500(4)	20.144(4)
c [Å]	29.236(6)	16.534(3)	16.432(3)	29.512(6)	19.284(4)
α [°]	90	90	90	90	90
β [°]	90	95.75(3)	96.35(3)	90	95.97(3)
γ [°]	90	90	90	90	90
V [Å^3]	2088.2(6)	1964.0(7)	1919.4(7)	4905.1(17)	4743.7(17)
Z	8	4	4	8	4
$D_{calcd.}$ [g cm^{-1}]	1.2356(4)	1.5787(6)	1.9245(7)	1.5626(5)	1.4733(5)
μ (Mo-K_α) [mm^{-1}]	0.075	1.016	7.106	0.984	2.675
F(000)	816	952	1080	2352	2120
Crystal size [mm]	0.24 × 0.16 × 0.09	0.45 × 0.25 × 0.18	0.40 × 0.1 × 0.05	0.18 × 0.09 × 0.04	0.14 × 0.09 × 0.02
θ range [°]	3.19–25.03	3.21–26.02	4.01–30.07	3.25–25.11	3.21–26.02
Index ranges	$-10 \le h \le 10$	$-10 \le h \le 9$	$-11 \le h \le 11$	$-10 \le h \le 10$	$-15 \le h \le 15$
	$-7 \le k \le 7$	$-17 \le k \le 17$	$-20 \le k \le 20$	$-23 \le k \le 23$	$-24 \le k \le 24$
	$-28 \le l \le 34$	$-20 \le l \le 20$	$-23 \le l \le 23$	$-34 \le l \le 35$	$-23 \le l \le 23$
Reflections collected	3522	24467	25780	8110	18157
Independent reflections	1833	3848	5620	4328	9318
R(int)	0.0169	0.0466	0.0407	0.0302	0.0224
Completeness to θ	99.2%	99.6%	99.7%	98.9%	99.6%
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	1833/0/166	3848/0/249	5620/0/244	4328/0/289	9318/0/614
Goodness-of-fit on F^2	1.069	1.044	1.099	1.041	1.062
Final *R* indices	R_1 = 0.0411	R_1 = 0.0254	R_1 = 0.0340	R_1 = 0.0368	R_1 = 0.0259
[$I > 2\sigma(I)$]	wR_2 = 0.1101	wR_2 = 0.0620	wR_2 = 0.0768	wR_2 = 0.0858	wR_2 = 0.0549
R indices	R_1 = 0.0550	R_1 = 0.0322	R_1 = 0.0471	R_1 = 0.0621	R_1 = 0.0352
(all data)	wR_2 = 0.1184	wR_2 = 0.0652	wR_2 = 0.0828	wR_2 = 0.0954	wR_2 = 0.0582
Absolute structure parameter	–	–	–	–	–
Largest difference peak/hole [e Å^{-3}]	0.089/–0.136	0.933/–0.643	3.496/–0.930	0.830/–0.643	1.184/–0.812

the SHELXS[31] program and refined by full-matrix least-squares with SHELXL-97.[31] CCDC-616194 (Hpyind), -616193 (**1**), -616192 (**2**), -616195 (**3**) and -616196 (**5**) 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.

Supporting Information (see footnote on the first page of this article): H,H-COSY and HMQC spectra for Hpyind and rhodium(III) complex **1**; dimeric unit of Hpyind within the crystal structure as additional ORTEP plot.

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