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An Ir–Pt Catalyst for the Multistep Preparation of Functionalized Indoles from the Reaction of Amino Alcohols and Alkynyl Alcohols

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Abstract: The 1,2,4-trimethyltriazolylidene (ditz) ligand allows the preparation of homo- and heterodimetallic complexes of Pt_2 and Ir–Pt. These two complexes have been characterized by means of spectroscopic and diffractommetric techniques. The catalytic activity of these complexes, together with that of other Pt-based compounds, has been explored in the cyclization–addition of alkynyl alcohols and indoles. The Ir–Pt complex $[\{PtI_2(py)\}(\mu\text{-ditz})\{IrI_2(Cp^*)\}]$ (py = pyridine; Cp* = pentamethylcyclopentadienyl) allows the combination of an iridium-mediated oxidative cyclization of 2-(*ortho*-aminophenyl)ethanol to form indoles, with a further step employing a Pt-based multistep reaction that functionalizes indoles. Our results show that the Ir–Pt complex is a very active catalyst in this new multistep preparation of functionalized indoles from the reaction of an amino alcohol with alkynyl alcohols.

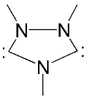
Keywords: carbenes • domino reactions • indoles • iridium • nitrogen heterocycles • N ligands • platinum

Introduction

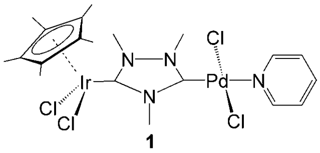
Over the course of the last decade, chemists have been trained to design processes with an increased awareness of the environmental impact, in an economically beneficial manner.[1] Within this context, click-chemistry methodologies[2] and tandem catalytic processes[3,4] have appeared as useful synthetic tools for the improvement of the efficient use of materials and energy. In the development of new approaches to organic molecules, the design of effective catalysts plays a decisive role. In general, well-defined catalysts are preferable to in situ-generated ones, because they often facilitate the investigation of the reaction mechanism and allow the further improvement of the catalytic activity by rational tuning of the properties of the catalyst. Also, in situ-generated catalysts often need an activation time, after the addition of an excess of the ligand (usually a phosphane), in order to allow the formation of the active catalyst.

In the search of more efficient methods for the preparation of complex organic architectures, there has been an increasing move towards finding multitopic catalysts that are active for a wide range of organic reactions, so that the combination of fundamental catalytic steps, involving simple and accessible substrates, can lead to sophisticated molecules. In nature, it has been shown that many enzymes contain two metal ions which operate cooperatively.[5] As a result, dinuclear complexes, containing two metals in close proximity, have become the subject of extensive investigation in order to design new bimetallic catalysts.[4,6]

For the last three years, we have focused part of our work on the design of well-defined, simple catalysts that facilitate a wide variety of organic transformations.[7] In this context, we have prepared a series of catalysts that are very active in several tandem catalytic processes.[8–11] Among these catalysts, those combining two significantly different metals allowed the combination of a number of mechanistically distinct catalytic reactions, typically mediated by each of the metals contained in the heterodimetallic unit.[9] For example, Ir–Pd complex **1** was able to catalyze a series of reactions typically catalyzed by Ir and Pd complexes, specifically the dehalogenation/transfer hydrogenation of haloacetophenones, the Suzuki coupling/transfer hydrogenation of *p*-bro-



ditz



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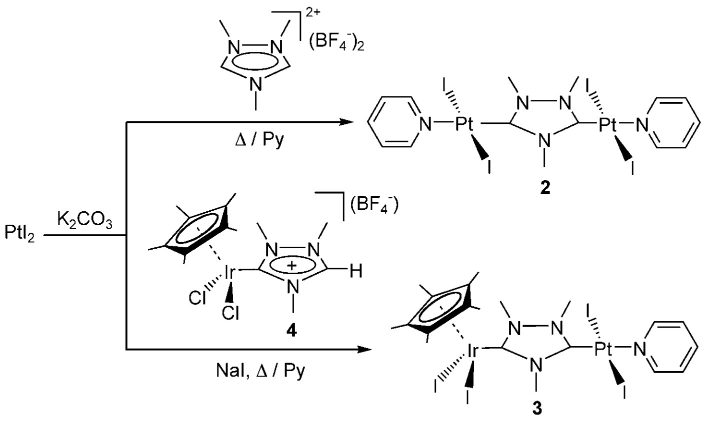
moacetophenone, and the Suzuki-coupling/α-alkylation of *p*-bromoacetophenone.[9]

Based on the benefits provided by complex **1** over other Ir–Pd catalysts and following our interest in the preparation of multitopic catalysts for tandem reactions, we now report on a heterodimetallic Ir^{III}–Pt^{II} complex with a 1,2,4-trimethyltriazolylidene (ditz) linker.[12] We have synthesized this complex with the aim of studying combinations of reactions typically catalyzed by Ir^{III} and Pt^{II}. With this in mind, we have combined the iridium-catalyzed oxidative cyclization of amino alcohols to form indoles[13] with the platinum-catalyzed multistep reaction of indoles with alkynyl alcohols.[14] The resulting tandem process comprises three consecutive reactions, namely the oxidative cyclization of an amino alcohol to form indole, the intramolecular hydroalkoxylation of an alkynyl alcohol to afford a cyclic enol ether, and the addition of a C–H bond of indole to the unsaturated moiety of the cyclic enol ether.

Results and Discussion

Synthesis and characterization of new complexes: Dimetallic complexes **2** and **3** were obtained as shown in Scheme 1. The reaction of PtI_2 with 1,2,4-trimethyltriazolium tetrafluoroborate and an excess of potassium carbonate, in refluxing pyridine afforded diplatinum complex **2** as an off-white crystalline solid, in high yield (75 %). Ir^{III}–Pt^{II} heterodimetallic complex **3**, was obtained by the reaction of PtI_2 with triazolium–ylidene–iridium complex **4**[11] and an excess of potassium carbonate, in refluxing pyridine. Complex **3** was isolated as an orange crystalline solid in moderate yield (41 %). Both complexes are stable in the solid state and can be handled in air.



Scheme 1. Py = pyridine

Complex **2** exhibits a characteristic ^{13}C NMR shift at 164.1 ppm for the carbene carbon, indicating the coordination of the NHC to the metal center. Heterodimetallic complex **3** shows two distinct resonances in this region due to the carbene carbon atoms bound to Pt (164.0 ppm) and Ir (155.5 ppm). The dimetallic nature of these two complexes was confirmed by high-resolution mass spectroscopy, in which the main peaks were at $m/z = 715.1340$ ($[M-I]^+$, **2**) and 1092.8806 ($[M-I]^+$, **3**).

A complete determination of the structures of **2** and **3** was achieved by means of X-ray diffraction studies. Figures 1 and 2 show the molecular diagrams of **2** and **3**, respectively.

The molecular structure of **2** (Figure 1) consists of two $PtI_2(py)$ fragments connected by a ditz bridge. The two metal fragments present a *trans*-conformation with respect to the iodide ligands. The two coordination planes about the metal centers are at an angle of 41.9°, slightly lower than that shown for the related dipalladium complex *trans*-$[\{PdCl_2(py)\}_2(\mu\text{-ditz})]$ (47.6°).[10] The two metal centers are quasi-coplanar with the plane of the azole ring, with a small deviation of 3.08° shown by the torsion angle Pt(1)-C(1)-N(2)-N(2A). The distance between the two platinum atoms is 5.96 Å and the Pt–C distance is 1.955 Å.

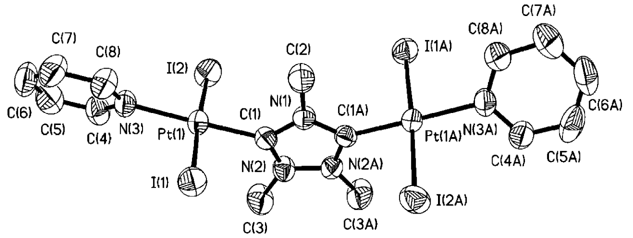


Figure 1. Molecular diagram of complex **2**. Ellipsoids at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–C(1) 1.955(7), Pt(1)–I(1) 2.5994(6), Pt(1)–I(2) 2.6030(7), Pt(1)–N(3) 2.085(6); C(1)-Pt(1)-N(3) 178.5(3), N(3)-Pt(1)-I(1) 91.99(17), C(1)-Pt(1)-I(2) 88.4(2), N(3)-Pt(1)-I(2) 91.50(17), I(1)-Pt(1)-I(2) 176.30(2), N(2)-C(1)-Pt(1) 127.3(5).

Compound **3** (Figure 2) is isostructural with our previously reported complex **1**,[9] with the only differences being that the Pd atom is replaced by Pt and the Cl atoms are replaced by I atoms. The molecule consists of a Cp^*IrI_2 (Cp^* = pen-

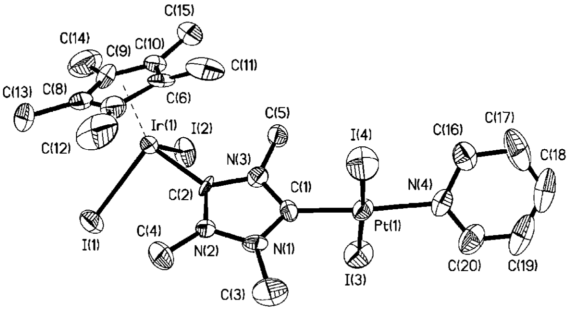
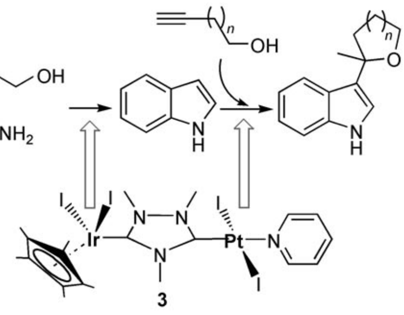


Figure 2. Molecular diagram of complex **3**. Ellipsoids at the 50 % probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(2) 2.011(10), Ir(1)–I(1) 2.7213(11), Ir(1)–I(2) 2.7195(11), Pt(1)–C(1) 1.932(12), Pt(1)–I(3) 2.6044(12), Pt(1)–I(4) 2.5987(12), Pt(1)–N(4) 2.077(11); C(2)-Ir(1)-I(1) 96.3(4), C(2)-Ir(1)-I(2) 91.4(3), C(1)-Pt(1)-I(3) 89.1(4), C(1)-Pt(1)-I(4) 88.0(4).

tamethylcyclopentadienyl) fragment connected to a PtI_2Py moiety by the triazolyldiylidene ligand. The structure of this complex allows a comparison between the bond lengths to Ir^{III} and Pt^{II} by the same ligand, within the same compound. These distances are 2.011 and 1.932 Å for $Ir^{III}–C_{carbene}$ and $Pt^{II}–C_{carbene}$, respectively. The two iodide ligands on the Pt fragment adopt a *trans* configuration. The distance between the two metal centers is 6.04 Å.

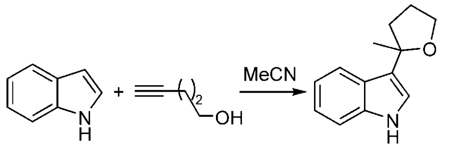
Catalytic studies: To study the catalytic abilities of complexes **2** and **3**, we decided to combine two reactions typically catalyzed by iridium and platinum complexes. For this purpose, we studied the combined oxidative cyclization of amino alcohols to form indoles (iridium catalyzed)[13] and the multistep reaction of indoles with alkynyl alcohols (platinum catalyzed), as shown in Scheme 2.[14] In the choice of these two reactions, we took into account the fact that, to design a tandem reaction, it is important to study the catalyst compatibility with the residual materials from the catalytic steps comprising the overall process. In principle, the reactions that we chose fulfill the requirements for compatibility in terms of solvent, temperature, and the nature of the bases used. In the selection of the reactions, we also took into account that indoles have become privileged structures in many research areas, owing to their applications in pharmaceuticals, fragrances, agrochemicals, pigments, and materials science,[15] and so a great deal of effort is currently devoted to the catalytic construction and functionalization of indole rings.[16]



Scheme 2.

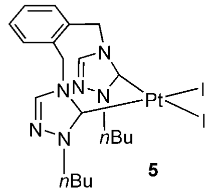
Firstly, we studied the multistep reaction of indoles with 4-pentyn-1-ol, which yields an indole derivative containing a five-membered cyclic ether at C3. This reaction was recently described by Cheng and co-workers,[14] who also proposed that the formation of the final product proceeds through a Pt-catalyzed cyclization of the alkynyl alcohol followed by the addition of indole to the resulting cyclic enol ether. Several gold catalysts are known to catalyze this multistep process,[17,18] although, unlike platinum, gold catalysts tend to facilitate the double addition of indole, generating bis(indolyl)alkane derivatives.[17] Table 1 shows representative data that we obtained for this reaction. To obtain a representative catalyst screening for this first set of experiments we used several platinum complexes, including catalyst **5**. The preparation and characterization of this bis(triazolylidene) complex of Pt (**5**) are detailed in the Experimental Section.

Table 1. Catalyst screening for the reaction of indole and pent-4-yn-1-ol.[a]



Entry	Catalyst[b]	Catalyst loading [mol %]	T [°C]	t [h]	Yield [%][c]
1[d,e]	$PtCl_2$	5	25	12	36
2[e]	**2**	5	25	12	73
3[e]	**5**	5	25	12	62
4	$PtCl_2$	5	80	0.5	84
5[d]	$PtCl_2$	5	25	2	22
6[d]	$PtCl_2$	1	80	1	77
7[d]	$PtCl_2$	1	25	27	46
8[d]	PtI_2	5	80	0.5	66
9[d]	PtI_2	1	80	1	80
10[d]	PtI_2	1	25	27	36
11	**2**	5	80	0.5	>95
12	**2**	1	25	27	58
13	**2**	5	25	2	71
14	**3**	5	80	0.5	>95
15	**3**	1	25	27	58
16	**3**	5	25	2	18
17	**5**	5	80	0.5	>95
18	**5**	1	25	27	75
19	**5**	5	25	2	46

[a] Reaction conditions: indole (0.3 mmol), 4-pentyn-1-ol (0.36 mmol), anisole (as an internal reference; 0.3 mmol), AgO_3SCF_3 (3 mol %) in CH_3CN (1.5 mL). [b] Based upon the amount of metal. [c] Yields determined by GC chromatography. [d] Without addition of AgO_3SCF_3. [e] Reactions carried out in toluene.



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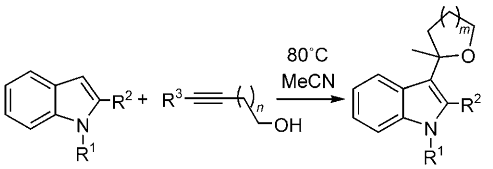
As can be seen from the data shown in Table 1, NHC-based platinum catalysts **2**, **3**, and **5** display better catalytic performances than $PtCl_2$ and PtI_2, although they need the addition of $AgSO_3CF_3$ in order to facilitate the process. Catalysts **2**, **3**, and **5** afford quantitative conversions to the final product, in only 30 min if the reaction is carried out at 80 °C, with a catalyst loading of 5 mol % (Table 1, entries 11, 14, and 17). The same catalysts afford moderate to high yields (58–75 %) if the reaction is performed at room temperature, with a catalyst loading of 1 mol %, although longer reaction times are needed (27 h).

These catalytic results prompted us to widen the variety of substrates used in this catalytic reaction. Table 2 shows representative data that we obtained for the reaction of a series of substituted indoles with substituted alkynyl alcohols. In general, catalyst **2** provided the best catalytic outcomes, affording almost quantitative yields for all of the reactions carried out with *N*-methylindole (Table 2, entries 1, 5, and 9). Heterodimetallic complex **3**, also afforded excellent outcomes in all of the reactions studied. We also established that the activity of complex **3** is also high if toluene is

Table 2. Catalytic addition reaction between indoles and alkynyl alcohols.[a]



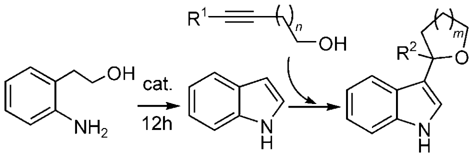
Entry	R^1	R^2	R^3	n	m	Catalyst[b]	t [h]	Yield [%][c]
1	Me	H	H	2	1	**2**	3	>99
2	Me	H	H	2	1	**5**	6	67
3	H	H	Me	1	1	**2**	6	80
4	H	H	Me	1	1	**5**	6	81
5	Me	H	Me	1	1	**2**	3	>99
6	Me	H	Me	1	1	**5**	3	>99
7	H	H	H	3	2	**2**	8	67
8	H	H	H	3	2	**5**	8	28
9	Me	H	H	3	2	**2**	12	93 (86)[d]
10	Me	H	H	3	2	**5**	12	52
11	H	Me	Me	1	1	**2**	15	60
12	H	Me	Me	1	1	**5**	15	60
13	Me	H	H	2	1	**3**	5	84
14[e]	H	H	Me	1	1	**3**	10	81
15	Me	H	Me	1	1	**3**	10	77 (72)[d]
16[e]	H	H	H	3	2	**3**	10	71
17	Me	H	H	3	2	**3**	10	74 (73)[d]
18	H	Me	Me	1	1	**3**	12	50 (46)[d]

[a] Reaction conditions: indole (0.3 mmol), alkynyl alcohol (0.36 mmol), silver triflate (3 %), and catalysts (1 mol %) in solvent (1.5 mL). Anisole was used as an internal standard (0.3 mmol). The solution was heated at 80 °C under aerobic conditions. [b] Based upon the amount of metal present. [c] Yields determined by GC chromatography. [d] Isolated yields in parenthesis. [e] Reactions carried out in toluene.

used as the solvent, with catalytic outcomes very close to those shown for reactions carried out in acetonitrile (see, Table 2, entries 14 and 16). This result is interesting because we have observed that toluene is a good solvent for the iridium-catalyzed oxidative cyclization of amino alcohols to form indole,[11] so the combination of the Pt- and Ir-catalyzed processes seems to be possible, at least in terms of solvent compatibility.

Having proved the activity of our Pt catalysts in the catalytic reaction between indoles and alkynyl alcohols, we thought that the combination of this multistep process with the oxidative cyclization of amino alcohols to form indoles might constitute a valuable illustration of the ability of our Ir–Pt complex **3** to incorporate a further step into the, already complex, catalytic reaction. Despite the great interest shown towards indole derivatives and the efforts that are currently being made towards the search for catalytic processes for the construction and functionalization of indole rings, we found very few examples in which functionalized indoles are obtained from multistep reactions employing amino alcohols.[11,19] The reactions were carried out in a single pot, following a sequential procedure. First we used 2-(*ortho*-aminophenyl)ethanol as the starting material to form indole and then we added the alkynyl alcohol, to provide the corresponding functionalized molecule. The reactions were carried out in toluene, at 110 °C, leaving 12 h for the first process (oxidative cyclization of the amino alcohol) and a variable time for the second (functionalization of indole). Table 3 summarizes a selection of representative results that we obtained for this tandem process.

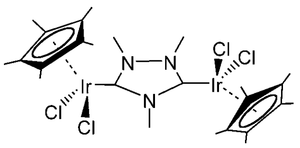
Table 3. Tandem cyclization of 2-(*ortho*-aminophenyl)ethanol and addition of an alkynyl alcohol.[a]



Entry	Catalyst ([mol %])[b]	R^1	R^2	n	m	Indole[c,d] [%]	t [h][e]	Yield [%][c]
1	**2** (2)	Me	Me	1	1	0	15	0
2	**3** (2)	Me	Me	1	1	77	15	74
3	**6** (2)	Me	Me	1	1	67	15	56
4	**2**+**6** (2)	Me	Me	1	1	51	15	44
5	**2**+**6** (2)	H	Me	2	1	nd	15	16
6	**2**+**6** (5)	H	Me	2	1	nd	12	35
7	[(IrCp*Cl$_2$)$_2$] (2)	Me	Me	1	1	38	15	29
8	[(IrCp*Cl$_2$)$_2$] (5)	Me	Me	1	1	nd	12	32
9	**3** (2)	H	Me	2	1	nd	15	60
10	**3** (5)	H	Me	2	1	nd	15	81 (77)
11[f]	**3** (2)	H	Me	3	2	nd	15	15
12[f]	**3** (5)	H	Me	3	2	nd	12	24
13[f]	**3** (2)	Pr	Pr	1	1	nd	24	80 (74)

[a] Reaction conditions: 2-(*ortho*-aminophenyl)ethanol (0.33 mmol), silver triflate (0.03 mmol), anisole (as an internal reference; 0.25 mmol) in toluene (800 μL) at 110 °C. After 12 h, alkynyl alcohol (0.38 mmol) was added. [b] Based upon the amount of metal. [c] Yields determined by GC chromatography. [d] Yield of the indole intermediate as determined before addition of the alkynyl alcohol. nd = not determined [e] Total time, referring to the two steps (the first step was always 12 h). [f] Reaction temperature of 80 °C.

As can be seen from the data shown in Table 3, catalyst **3** provided good yields of the functionalized indoles when different alkynyl alcohols were used (yields in the range 60–81 %). These data are remarkable, especially if we take into account the complexity of the overall process. As expected, diplatinum complex **2** did not afford the formation of the final products, due to its inability to facilitate the oxidative cyclization of the amino alcohol. Furthermore, a mixture of the two homodimetallic complexes of Pt (**2**) and Ir (**6**)[11], afforded a much lower yield than that provided by heterodimetallic complex **3** (compare Table 3, entries 4–6 with Table 3, entries 2, 9 and 10). This result is comparable with the catalytic outcomes shown by other ditz-based heterodimetallic complexes reported by us when compared to mixtures of their homodimetallic counterparts[9,11,20] and supports the idea that some catalytic cooperativity between the



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two vicinal metals may be at work. The results shown for iridium complexes **6** and [$(IrCp^{*}Cl_2)_2$], which afford low (ca. 30%, for [$(IrCp^{*}Cl_2)_2$], Table 3, entries 7 and 8) to moderate (56%, for complex **6**, Table 3, entry 3) yields of the final product, are remarkable, since, in contrast to what we expected, they demonstrate that these complexes also show activity in the final step of the reaction. Remarkably, the activity of complex **3** is entirely unaffected by the addition of metallic Hg,[21] lending support to a homogeneous reaction mechanism.

Conclusion

Herein, we have prepared two new dimetallic complexes containing the dicarbene ligand ditz. The preparation of these two new complexes illustrates the high versatility of this ditopic ligand. The easy access to Ir–Pt heterodimetallic complex **3** allowed us to study a tandem process employing the combination of mechanistically distinct processes that are typically catalyzed by Ir or Pt. We have first shown that all of our Pt-based complexes show high activity in the cyclization–addition reactions of alkynyl alcohols with indoles. The presence of the Ir-fragment in complex **3** allows the addition of a further step to this reaction, since it can then be started from 2-(*ortho*-aminophenyl)ethanol, which is transformed into indole by an Ir-mediated oxidative cyclization process and then reacts with the alkynyl alcohol in a Pt-mediated reaction.

The ability of Ir–Pt complex **3** to perform this combined reaction confirms the wide ranging applicability of ditz-based heterodimetallic complexes for the design of new and complex tandem processes. The preparation of substituted indoles from the direct reaction of 2-(*ortho*-aminophenyl)-ethanol and alkynyl alcohols is an unprecedented process that may have some industrial applications. As we have previously shown for other heterodimetallic ditz-based complexes,[9,11] the use of **3** provides better catalytic outcomes than the use of mixtures of the corresponding homodimetallic catalysts (**2** and **6**), suggesting that some catalytic cooperativity may be at work between the two vicinal metals. The results presented in this work, together with our previously reported results on the use of the ditz ligand for the preparation of ditopic catalysts,[9,11,20] confirm the abundant applications of this ligand for the preparation of catalysts suitable for mediating complicated tandem catalytic processes. In a context in which the search for reactions with a reduced environmental impact in an economically beneficial manner is one of the first priorities of synthetic chemistry, we strongly believe that the design of well-defined, effective, multitopic catalysts constitutes a valuable route of exploration with foreseeable profitable results.

Experimental Section

General procedures: 1,2,4-Trimethyltriazolium tetrafluoroborate,[22] *o*-xylenebis(*N*-*n*-butyl)triazolium diiodide[23] and complex **6**[11] were prepared according to literature procedures. All other reagents and solvents were used as received from commercial suppliers. Synthesis and catalytic experiments were carried out under aerobic conditions, without solvent pre-treatment. NMR spectra were recorded on Varian spectrometers operating at 300 or 500 MHz (^{1}H NMR) and 75 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm and J in Hertz). NMR spectra were recorded at room temperature in $CDCl_3$, unless otherwise stated. A QTOF I (quadrupole–hexapole–TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. The drying gas, as well as the nebulizing gas, was nitrogen at a flow of 400 and 80 $L\,h^{-1}$, respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. A capillary voltage of 3.5 kV was used in the positive scan mode and the cone voltage was set to 30 V. Mass calibration was performed by using a solution of sodium iodide in isopropanol/water (50:50) from $m/z = 150$ to 1000 a.m.u. Sample solutions ($\approx 1\times10^{-4}$ M) in dichloromethane/methanol (50:50) were infused through a syringe pump directly connected to the interface at a flow rate of 10 $\mu L\,min^{-1}$. A solution of 3,5-diiodo-L-tyrosine (1 $\mu g\,mL^{-1}$) was used as the lock mass. Elemental analyses were carried out on a EuroEA3000 Eurovector Analyser. A gas chromatograph GC-2010 (Shimadzu) equipped with an FID and a Teknokroma (TRB-5MS, 30 m x 0.25 mm x 0.25 μm) column was used. A gas chromatograph/Mass spectrometer GCMS-QP2010 (Shimadzu) equipped with a Teknokroma (TRB-5MS, 30 m x 0.25 mm x 0.25 μm) column was also used.

Synthesis of 2: A mixture of 1,2,4-trimethyltriazolium tetrafluoroborate (60 mg, 0.21 mmol), PtI_2 (180 mg, 0.42 mmol), and K_2CO_3 (221 mg, 1.6 mmol) was heated at reflux for three hours in pyridine (3 mL). The reaction mixture was then filtered through Celite, and the solvent was removed under vacuum. Pure compound **2** (170 mg, 70%) was obtained as a light yellow solid after recrystallization from dichloromethane/*n*-hexanes (1:9; 2 mL×2). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 8.91$ (d, $^{3}J_{H,H} = 5.0$ Hz, 4H; Py), 6.55 (t, $^{3}J_{H,H} = 7.5$ Hz, 2H; Py), 6.27 (t, $^{3}J_{H,H} = 6.5$ Hz, 4H; Py), 4.63 (s, 3H; NCH_3), 3.38 ppm (s, 6H; NCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 164.1$ (NCN–Pt), 153.5, 138.2, 125.2 (Py), 40.4, 37.0 ppm ($-CH_3$); ES-MS (25 V): m/z: 1189.1 $[M+Na]^+$; ESI-TOF-MS (positive mode): m/z calcd (monoisotopic peak): 715.1335; found: 715.1340; $\varepsilon_r = 0.7$ ppm.

Synthesis of 3: A mixture of compound **4** (120 mg, 0.2 mmol), PtI_2 (100 mg, 0.22 mmol), NaI (150 mg, 1 mmol), and K_2CO_3 (83 mg, 0.6 mmol) was heated for three hours in pyridine (3 mL) at 80 °C. The reaction mixture was then filtered through Celite and the solvent was removed under vacuum. The excess of salt was eliminated by dissolving the crude in dichloromethane and filtering the solution. Pure compound **3** (110 mg, 41%) was obtained as a light yellow solid after precipitation from *n*-hexanes. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 8.90$ (d, $^{3}J_{H,H} = 5.0$ Hz, 2H; Py), 7.75 (t, $^{3}J_{H,H} = 7.0$ Hz, 1H; Py), 7.33 (t, $^{3}J_{H,H} = 6.5$ Hz, 2H; Py), 4.27 (s, 3H; NCH_3), 4.24 (s, 3H; NCH_3), 4.23 (s, 3H; NCH_3), 1.79 ppm (s, 15H; $C_5(CH_3)_5$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.0$ ($C_{carbene}$–Ir), 155.5 ($C_{carbene}$–Pt), 153.5, 138.1, 125.2 (Py), 91.6 ($C_5(CH_3)_5$), 45.4 (NCH_3), 41.8 (NCH_3), 8.9 ppm ($C_5(CH_3)_5$); ESI-TOF-MS (positive mode): m/z calcd (monoisotopic peak): 1092.8785; found: 1092.8806; $\varepsilon_r = 1.92$ ppm.

Synthesis of 5: A mixture of *o*-xylenebis(*N*-*n*-butyl)triazolium diiodide (200 mg, 0.47 mmol), PtI_2 (210 mg, 0. 47 mmol), and NaOAc (77 mg, 0.94 mmol) was heated at reflux for five hours in acetonitrile (5 mL). The reaction mixture was then filtered through Celite and the solvent was removed under vacuum. Pure compound **5** (275 mg, 73%) was obtained as a white crystalline solid after recrystallization from acetone/diethyl ether (1:9). ^{1}H NMR (500 MHz, CD_3CN): $\delta = 8.42$ (s, 2H; NCH), 7.77 (m, 2H; Ph), 7.51 (m, 2H; Ph), 6.68 (d, $^{2}J_{H,H} = 14.5$ Hz, 2H; CH_2), 5.15 (d, $^{2}J_{H,H} = 15.0$ Hz, 2H; CH_2), 4.67 (m, 2H; CH_2, *n*Bu), 4.18 (m, 2H; CH_2, *n*Bu), 2.02 (m, 2H; CH_2, *n*Bu), 1.97 (m, 2H; CH_2, *n*Bu), 1.46 (m, 4H; CH_2, *n*Bu), 0.98 ppm (t, $^{3}J_{H,H} = 7.5$ Hz, 6H; CH_3, *n*Bu); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 156.6$ (NCH), 143.5 ($J_{Pt,C} = 203.0$ Hz, $C_{carbene}$–Pt), 135.6, 133.0, 131.7 (Ph), 52.7 (CH_2), 49.13, 31.1, 20.7, 14.0 ppm (*n*Bu); ES-MS

(25 V): m/z: 716.0 $[M{-}I{+}CH_3CN]^+$; ESI-TOF-MS (positive mode): m/z calcd (monoisotopic peak): 715.1335; found: 715.1340; $\varepsilon_r = 0.69$ ppm.

Cyclization–addition reaction of indole with alkynyl alcohol: A capped vessel containing a stirrer bar was charged with indole (0.3 mmol), alkynyl alcohol (0.36 mmol), silver triflate (3 %), anisole (as an internal reference; 0.3 mmol), and catalyst (1 %) in acetonitrile (1.5 mL). The solution was heated to 80 °C for the appropriate length of time. During the reaction, yields and conversions were determined by GC chromatography. Products and intermediates were characterized by GC/MS. Isolated products were characterized by ^{1}H and ^{13}C NMR spectroscopy after purification by column chromatography using mixtures of *n*-hexanes and ethyl acetate.

Sequential oxidation–cyclization of amino alcohol into indole and functionalization with alkynyl alcohol: A capped vessel containing a stirrer bar was charged with 2-(*ortho*-aminophenyl)ethanol (0.33 mmol), silver triflate (0.03 mmol), anisole (as an internal reference; 0.3 mmol), and catalyst (2 %) in toluene (800 µL). The solution was heated to 110 °C for the appropriate length of time. After complete conversion to the indole, the alkynyl alcohol (0.38 mmol) was added and the final solution was stirred, at the same temperature, for an additional 3 h. During the reaction, yields, and conversions were determined by GC chromatography. Products and intermediates were characterized by GC/MS. Isolated products were characterized by ^{1}H and ^{13}C NMR spectroscopy after purification by column chromatography using mixtures of *n*-hexanes and ethyl acetate.

X-ray diffraction studies: Single crystals of **2** and **3** were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. Space group assignment was based on systematic absences, *E* statistics and successful refinement of the structures. The structures were solved by direct methods with the aid of successive difference Fourier maps and were refined by using the SHELXTL 6.1 software package.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined by using a riding model. Details of the data collection, cell dimensions and structure refinement are given in Table 4. The diffraction frames were integrated by using the SAINT package.[25] CCDC-774939 (**2**) and -774940 (**3**) 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.

Table 4. Crystallographic data and structure refinement for complexes **2** and **3**.[a]

	2	3
formula	$C_{15}H_{19}I_4N_5Pt_2$	$C_{20}H_{29}I_4IrPtN_4$
M_r	1167.13	1305.29
T [K]	293(2)	293(2)
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*P*21/*n*
a [Å]	26.404(3)	14.7970(8)
b [Å]	10.9836(12)	9.2108(5)
c [Å]	8.9600(10)	23.6378(13)
α [°]	90	90
β [°]	90.232(2)	98.665(1)
γ [°]	90	90
V [Å^3]	2598.5(5)	3184.9(3)
Z	4	4
ρ_{calcd} [Mg m^{-3}]	2.983	2.722
$\mu(Mo_{K\alpha})$ [mm^{-1}]	15.517	12.624
total/unique reflns.	2985/2423	7304/4882
R_{int}	0.0297	0.0429
parameters/restraints	119/0	314/0
R/R_w ($I > 2\sigma$)	0.0324/0.0750	0.0535/0.1168
GOF	1.037	1.068
Min/max residual density [e Å^{-3}]	−1.108/1.266	−1.737/2.824

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for all $I > 3\sigma(I)$; $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

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