New 1,2,3-triazole ligands through click reactions and their palladium and platinum complexes†

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The new ligands, 1-(4-isopropyl phenyl)-4-(2-pyridyl)-1,2,3-triazole, **1** and 1-(mesityl)-4-(2-pyridyl)-1,2,3-triazole, **2** were prepared by the reactions of the respective azides with 2-ethynylpyridine following the "click method". These ligands together with the reported ligands 1-(phenyl)-4-(2-pyridyl)-1,2,3-triazole, **3** and 1-(benzyl)-4-(2-pyridyl)-1,2,3-triazole, **4** were reacted with palladium and platinum precursors to give mononuclear *cis*-dichloropalladium and platinum complexes containing the triazole ligands. Structural characterisation of the free ligand **3** shows that the central N–N bond in the triazole ring has double bond character and hence is best described as an "azo-like" N–N double bond. The pyridine ring in **3** has an almost "*anti*" conformation with respect to the central triazole ring. The metal centers bind to the ligands through the pyridine N and a triazole N atom. The metal–N(triazole) distances are shorter than the metal–N(pyridine) distances. Cyclic voltammograms of the ligands show reduction processes that appear at extreme negative potentials. Coordination of metal centers induces huge anodic shifts of the reduction potentials due to σ-polarisation by the metal centers. UV/Vis spectra of the ligands and complexes are also discussed. The properties of such chelating triazole ligands towards palladium and platinum centers is being compared and contrasted to the widely used 2,2′-bipyridine ligand.

Introduction

The 1,3-dipolar cycloaddition reaction between azides and terminal alkynes was first systematically studied by Huisgen several decades ago.[1,2] The copper catalysed form of this reaction has been renamed as the "click reaction".[3,4] These reactions demonstrate high regioselectivity to give the 1,4-linked triazoles in excellent yields. Since the discovery of the click reaction, this method has found use in diverse areas of chemistry such as dendrimers and polymers,[5-7] drug discovery,[8] material science[9] and bioconjugation,[10] to name but a few. The same reaction has also been used to generate metal responsive fluorophores.[11] Even though substituted 1,2,3-triazoles should be good candidates for acting as ligands in coordination chemistry, their use as ligands has been much less explored in comparison to their 1,2,4-counterparts. There have been some recent reports on the use of such ligands as "analogues of terpyridine and bipyridine".[12-15] Copper complexes have been reported with potentially tetradentate 1,2,3-triazole ligands where the question of the mechanism of the click reaction was also addressed.[16] Additionally, rhenium complexes of such ligands have been studied in the therapeutic and photophysical context.[17,18] To the best of our knowledge the only report of platinum complexes with such 1,2,3-triazole ligands are the ones where such ligands act in a monodentate fashion or the donor substituents on the triazole ring are aliphatic.[19,20] Complexes of *cis*-dichloroplatinum with nitrogen co-ligands are interesting for a variety of reasons such as tumor therapy,[21] luminescence in solid state and solution[22] and as catalysts and pre-catalysts for C–H bond activation.[23,24] In recent years *cis*-dichloropalladium complexes have found extensive use as catalysts and pre-catalysts in various organic transformations.[25] 2,2′-Bipyridine is the prototypical nitrogen ligand that has been extensively used for many of the research fields mentioned above. The click method provides an extremely convenient route for the synthesis of (2-pyridyl)-substituted 1,2,3-triazoles which could potentially be used as "2,2′-bipyridine analogues".[15] In comparison to 2,2′-bipyridine it is relatively easy to vary the steric and electronic properties of such triazole ligands. In addition platinum complexes of "non-click" 1,2,3-triazoles have been studied for a variety of purposes.[26] With this background in mind, we prepared two new substituted triazoles 1-(4-isopropyl phenyl)-4-(2-pyridyl)-1,2,3-triazole, **1** and 1-(mesityl)-4-(2-pyridyl)-1,2,3-triazole, **2** (Scheme 1 and 2). These ligands together with the reported ligands 1-(phenyl)-4-(2-pyridyl)-1,2,3-triazole, **3**[15] and 1-(benzyl)-4-(2-pyridyl)-1,2,3-triazole, **4**[18] (Scheme 1) were reacted with $Pd(COD)Cl_2$ (COD = 1,5-cyclooctadiene) and $Pt(dmso)_2Cl_2$ respectively to give the complexes **1a–4a** and **1b–4b** (Scheme 3). Herein we present the detailed synthesis and characterisation of the ligands and complexes together with the crystal structures of **3**, **1a** and **3b**. The electrochemical as well as the UV/Vis spectroscopic results of all the compounds are also reported and discussed. These studies are presented to compare the properties of the metal complexes of such triazole ligands with their known 2,2′-bipyridine analogues. In addition, electrochemical and spectroscopic studies on these complexes also help in probing the effects of substituents and of metal complexation on various properties of such ligands.

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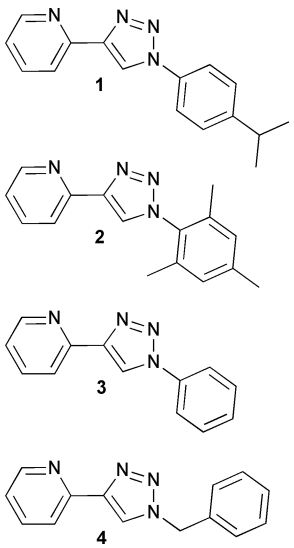
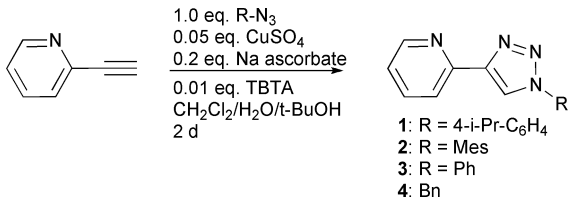
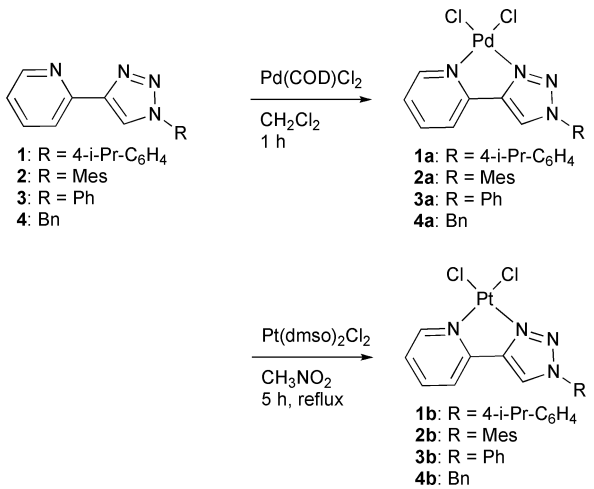
† Electronic supplementary information (ESI) available: ^1H NMR and ^{13}C NMR spectra of **2**; UV/vis spectra of **1a–4a**. CCDC reference numbers 733411–733413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b910660j



Scheme 1 Triazole ligands used in this work.



Scheme 2 Synthesis of triazole ligands.



Scheme 3 Synthesis of metal complexes.

Results and discussion

Synthesis and structures

Ligands **1** and **2** were prepared by the Cu(I) catalysed 1,3-dipolar cycloaddition ("click method") from the reactions of the respective azide derivatives with 2-ethynylpyridine. Thus the reactions of 4-isopropyl-phenylazide or mesitylazide, respectively, with 2-ethynylpyridine in the presence of $CuSO_4$, sodium ascorbate and TBTA (tris[(1-benzyl-1H-1,2,3-triazole-4-yl)methyl]amine) in a mixture of CH_2Cl_2–H_2O–t-BuOH at room temperature gave **1** and **2** in excellent yields (Scheme 2). These reactions are highly regioselective towards the 4-(2-pyridyl) isomer as has previously been observed with such click reactions.[14,15,18] The regioselectivity was also unambiguously determined through the crystal structure of ligand **3** (*vide infra*), the synthesis of which was previously reported.[15] The ligands were characterised by ^{1}H- and ^{13}C NMR spectroscopy, mass spectroscopy and by elemental analysis. In the ^{1}H NMR, the C–H proton of the triazole ring is characteristic and appears relatively downfield as a singlet (see experimental) for all the ligands. Thus this method provides a facile route to the synthesis of a variety of pyridyl substituted triazole ligands with the substituents on the triazole ring being limited only by the availability of the corresponding azide compound.

Complexes **1a–4a** were synthesised by the reactions of $[Pd(COD)Cl_2]$ with the respective ligands in CH_2Cl_2 at room temperature. The yields were almost quantitative. For the complexes **1b–4b** the precursor $[Pt(dmso)_2Cl_2]$ was used and the reactions were carried out under reflux in nitromethane (Scheme 3). Much higher reaction times and temperature were necessary for the synthesis of the platinum complexes as compared to the palladium complexes. Although the triazole ligands can in principle bind to a metal center through either the N2 or N3 atoms of the triazole ring, substitution of a 2-pyridyl group at the 4-position of the triazole ring results in preferential binding to the N3 atom with the formation of a five membered chelate ring. The complexes were characterised by ^{1}H NMR spectroscopy and elemental analyses. In the ^{1}H NMR spectra of the complexes **1b–4b**, ^{195}Pt satellites were observed for the 5-triazole*H* and 6-pyridyl*H* protons (see experimental). This unambiguously proves the binding of the platinum centers to the ligands.

The molecular structure of ligand **3** was determined by single crystals X-ray diffraction (Fig. 1). Crystallographic data are presented in Table 1 and selected bond lengths are reported in Table 2.

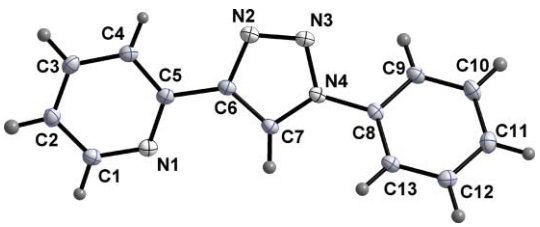


Fig. 1 ORTEP of the molecular structure of **3**. Ellipsoids include 30% of electron density.

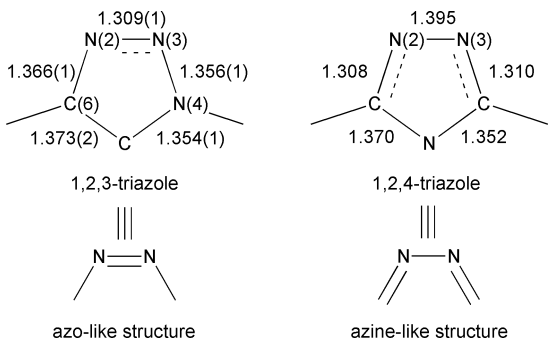
In the structure of **3**, the pyridine ring has an almost "*anti*" conformation with respect to the triazole ring (Fig. 1). The angle between the least square planes of the triazole and pyridine rings is 17.8(1)°. This value is comparable to what has been previously observed for other such 1,2,3-triazole ligands.[18] The twisting of the phenyl ring with respect to the triazole ring is about 27.8(1)°. As has been observed previously,[18] the N2–N3 distance of the 1,2,3-triazole at 1.309(2) Å is shorter than the N2–C6 and N3–N4 bonds (1.366(1) and 1.356(1) Å respectively). For the corresponding 1,2,4-triazoles, the N2–N3 bonds are longer than those of the adjacent two bonds. This suggests that the 1,2,3-triazoles have an azo character while 1,2,4-triazoles have an azine character as has been observed by Obata *et al.* for ligand **4** (Scheme 4).[18]

Table 1 Crystallographic details

	3	1a	3b
Chemical formula	$C_{13}H_{10}N_4$	$C_{16}H_{16}Cl_2N_4Pd$	$C_{13}H_{10}Cl_2N_4Pt$
M_r	222.25	441.63	488.24
Cell setting	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/c$
Temperature/K	100(2)	173(2)	173(2)
a/Å	5.7757(2)	6.8228(2)	7.5513(3)
b/Å	19.3231(6)	18.1883(6)	19.237(1)
c/Å	9.7917(2)	27.2193(9)	9.6692(7)
β/°	99.295(2)	90.00	102.301(4)
V/Å^3	1078.45(6)	3377.78(19)	1372.34(13)
Z	4	8	4
D_x/Mg m^{-3}	1.369	1.737	2.363
Radiation type	Mo Kα	Mo Kα	Mo Kα
μ/mm^{-1}	0.087	1.418	10.607
Crystal size/mm	0.3 × 0.1 × 0.05	0.1 × 0.02 × 0.02	0.14 × 0.08 × 0.08
Meas., indep. and obsvd refl.	5135, 2660, 2095	7108, 3868, 2522	4587, 2773, 2104
$R[F^2 > 2\sigma(F^2)]$	0.038	0.043	0.035
w$R(F^2)$	0.093	0.127	0.098
S	1.02	1.07	1.08
No. of parameters	195	210	181
R_{int}	0.023	0.057	0.039
θ_{max}/°	28.3	27.5	26.4
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.27, –0.21	0.67, –1.31	1.43, –1.47

Table 2 Selected bond lengths in Å

	3	1a	3b
N2–N3	1.309(1)	1.312(6)	1.33(1)
N3–N4	1.356(1)	1.349(5)	1.344(9)
N4–C7	1.354(1)	1.343(6)	1.36(1)
N2–C6	1.366(1)	1.364(6)	1.35(1)
C6–C7	1.373(2)	1.359(7)	1.36(1)
C5–C6	1.470(2)	1.464(7)	1.48(1)
M–N1		2.055(4)	2.044(7)
M–N2		2.007(4)	1.987(7)
M–Cl1		2.264(1)	2.283(2)
M–Cl2		2.285(1)	2.291(2)



Scheme 4 Differences in bonding pattern in isomeric triazole compounds. For bond lengths of the azine-like structure see Cingi *et al*.[27]

The molecular structures of complexes **1a** and **3b** were also determined (Fig. 2 and 3). Crystal data and details of the structure determination are listed in Table 1. Selected bond lengths and angles are given in Table 2 and 3. The coordination mode of the metal centers to the substituted 1,2,3-triazole ligands is very similar to that of the 2,2′-bipyridine derivative. The platinum and palladium centers bind to the 1,2,3-triazole ligands through the pyridine-N atom and the N2 atom of the triazole ring. In both

Table 3 Selected bond angles (°)

	1a	3b
N1–M–N2	80.6(2)	80.0(3)
N1–M–Cl2	94.4(1)	94.8(2)
N2–M–Cl1	94.0(1)	94.7(2)
Cl1–M–Cl2	91.01(5)	90.8(1)
ω^a	52.3(2)	32.2(3)

[a] Dihedral angle between the triazole ring and the free substituent (angle between the mean planes defined by the atoms of (a) the phenyl and (b) the triazole ring).

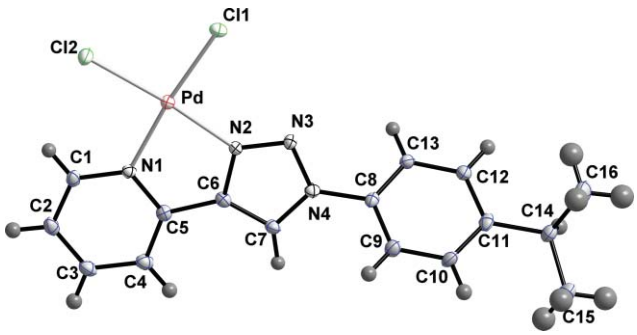


Fig. 2 ORTEP of the molecular structure of **1a**. Ellipsoids include 30% of electron density.

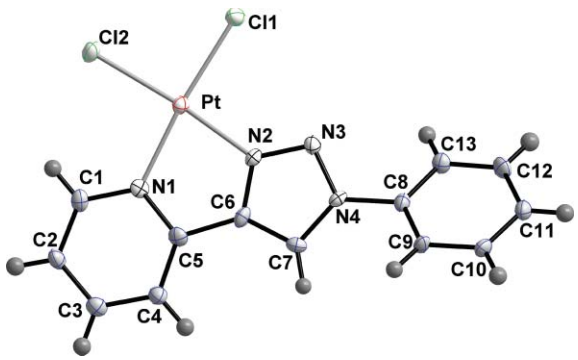


Fig. 3 ORTEP of the molecular structure of **3b**. Ellipsoids include 30% of electron density.

structures, the slightly distorted square planar coordination is completed by two chlorides. The chelating N1–M–N2 bite angles (80.6(2) and 80.0(3)° respectively for **1a** and **3b**) are slightly shorter in both complexes compared to the other angles around the metal centers. The M–N(triazole) distances are shorter than the M–N(pyridine) distances. This is due to the strong electron-donating properties of the 1,2,3-triazole ring in comparison to the pyridine ring. Similar trends are known for metal complexes of other azole ligands containing a 2-pyridyl substituent.[18,28] Consistently with the enhanced *trans* influence of N2 with respect to N1, the M–Cl2 distances are slightly longer than the M–Cl1 distances. The N2–N3 bond distance inside the 1,2,3-triazole ring is slightly longer in the metal complexes (particularly **3b**) compared to the free ligand. This is possibly due to π back donation from the metal centers into the triazole ring. Such elongation of the N–N double bond has been previously observed for metal complexes containing substituted "azo" ligands.[29] While the pyridyl–MCl_2–triazole parts in **1a** and **3b** are almost co-planar, the angle between the phenyls mean

Table 4 Electrochemical and UV/vis spectroscopic data

Compound	E_{pc} [a]	λ [b]
1	−2.80[c]	288
2	−2.83[c]	281
3	−2.86[c]	287
4	−2.78[c]	281
1a	−1.25	273, 379
2a	−1.23	275, 381
3a	−1.17	269, 380
4a	−1.28	280, 373
1b	−2.11	266, 337
2b	−2.16	266, 337
3b	−2.13	264, 335
4b	−2.15	261, 335
$Pt(bpy)Cl_2$[d]	−1.06	312, 324, 389
$Pt(abpy)Cl_2$[e]	−0.54	395, 516

[a] Cathodic peak potential in V for irreversible reduction in CH_2Cl_2/0.1 M Bu_4NPF_6. The ferrocene/ferrocenium couple was used as internal standard. [b] Wavelength in nm. Measurements in CH_2Cl_2. [c] Measurements in DMF. [d] Half wave potential for reversible reduction. Measurements in DMF. Ref. 31. [e] Half wave potential for reversible reduction at −50 °C. Ref. 27.

planes and the triazole ones are 52.3(2) and 32.2(3)°, respectively, for **1a** and **3b**. The 4-isopropylphenyl or the phenyl substituents in **1a** and **3b** twist apparently in order to minimise the steric repulsion between the C–H bonds of the C7 and C9 atoms.

Cyclic voltammetry

Cyclic voltammetry was employed in order to probe the redox properties of the ligands and the metal complexes. The ligands had to be measured in DMF because of their extremely negative reduction potentials. For instance ligand **3** shows an irreversible reduction at −2.86 V in DMF/0.1 M Bu_4NPF_6 *vs.* ferrocene/ferrocenium (Table 4). The effect of the substituents on the phenyl rings of the triazole ligands on the redox potentials is negligible and all the ligands **1–4** show very similar reduction potentials. Such high reduction potentials for 1,2,3-triazole ligands have been observed previously.[12]

The palladium complexes **1a–4a** show an irreversible reduction process at around −1.2 V in CH_2Cl_2/0.1 M Bu_4NPF_6 *vs.* ferrocene/ferrocenium (Fig 4 and Table 4). The reversibility of this process did not improve on lowering the temperature or varying the scan rates. Metal–halide bonds are known to be labile on reduction[30] and such reduction induced bond activation can sometimes be useful for certain kinds of catalytic activation.[31,32] The reduction potential for complexes **1a–4a** show huge metal-

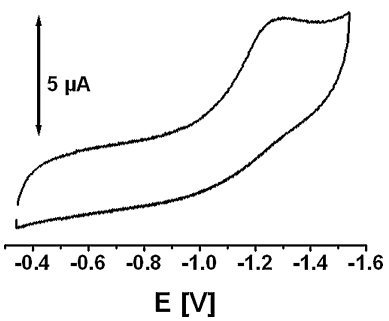


Fig. 4 Cyclic voltammogram of **4a** in CH_2Cl_2/0.1 M Bu_4PF_6 at 295 K.

coordination induced anodic shifts compared to the free ligands (Table 4). This is because of the excellent σ-acceptor capacity of the $[PdCl_2]$ fragment. The platinum complexes **1b–4b** show an irreversible reduction process at around −2.1 V in CH_2Cl_2/0.1 M Bu_4NPF_6 *vs.* ferrocene/ferrocenium (Fig 5 and Table 4). Just like for the palladium complexes the reversibility did not improve upon changing the temperature or scan rates. The reduction potentials for the platinum complexes are also anodically shifted compared to those of the free ligands. However, the anodic shift in this case is much smaller than that of the palladium complexes. This has to do with the much better σ-acceptor capacity of the $[PdCl_2]$ fragment compared to the $[PtCl_2]$ fragment in such complexes. The influence of the substituents on the triazole ring on the reduction potentials of both the palladium as well as platinum complexes is negligible.

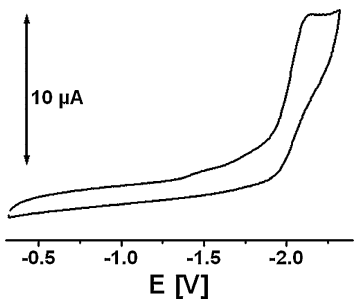


Fig. 5 Cyclic voltammogram of **4b** in CH_2Cl_2/0.1 M Bu_4PF_6 at 295 K.

On comparing the reduction potentials of complexes **1b–4b** with those of $Pt(bpy)Cl_2$[33] and $Pt(abpy)Cl_2$[29] (bpy = 2,2′-bipyridine, abpy = 2,2′-azobispyridine, Table 4) one sees that the reduction potentials for the present triazole containing complexes are more negative than those of $Pt(bpy)Cl_2$ and $Pt(abpy)Cl_2$ with the complex $Pt(abpy)Cl_2$ being the easiest to reduce (least negative reduction potential). These results point to the fact that the π* LUMO for complexes **1b–4b** are energetically higher than the LUMOs of $Pt(bpy)Cl_2$ and $Pt(abpy)Cl_2$.

UV/Vis spectroscopy

Ligands **1–4** show a π–π* transition between 281–288 nm (Fig. S3† and Table 4). The strongly shifted reduction potentials evidenced for the metal complexes would point to a relatively low lying π* orbital. Despite this fact, the absorption bands for the complexes appear at quite high energies. This is probably due to the strong stabilisation of the predominantly $[MCl_2]$ centered HOMOs in these complexes. Such effects have been observed previously for the corresponding metal complexes with the bpy and abpy ligands.[29,33] All the complexes show two main features in their absorption spectrum (Fig. 6 and S4† and Table 4). The long wavelength band (*e.g.* 379 nm for **1a**) is tentatively assigned to a mixture of metal-to-ligand charge transfer (MLCT) with some contribution from halide-to-ligand (XLCT) charge transfer. The next highest energy transition (*e.g.* 273 nm for **1a**) is most likely a π → π* transition centered on the triazole ligand. The transitions for the palladium complexes **1a–4a** are shifted to lower energies compared to those of the corresponding platinum complexes **1b–4b** (Fig. 6 and Table 4). This is in keeping with the lower lying LUMO for the palladium complexes as compared to the platinum complexes. The long wavelength bands for the $Pt(bpy)Cl_2$ and $Pt(abpy)Cl_2$

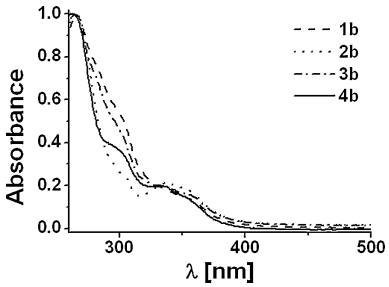


Fig. 6 UV/Vis spectra of **1b–4b** in CH_2Cl_2.

complexes appear at lower energies compared to the present complexes with triazole ligands.[29,33] This can be rationalised by the lower energy π* LUMO for the Pt(bpy)Cl_2 and Pt(abpy)Cl_2 complexes compared to the complexes **1b–4b**.

Conclusions

Using the increasingly popular "click method" we have synthesised two new 1,2,3-triazole containing ligands. Reactions of these and other previously reported ligands with the appropriate metal precursors gave the palladium complexes **1a–4a** and the platinum complexes **1b–4b**. Structural characterisation of some of the complexes show that the bond between the metal centers and the triazole-N is shorter compared to that between the metal centers and the pyridine-N. The reduction processes for the free ligands as well as the metal complexes are irreversible. However, large metal coordination induced anodic shifts were observed for the reduction of the metal complexes as compared to those of the free ligands. The present studies show the utility of such substituted 1,2,3-triazole compounds, obtained through the "click method", as excellent ligands in coordination chemistry. Future efforts will be dedicated to tuning the properties of such ligands and their metal complexes by varying the electronic properties of such ligands.

Experimental

General

All solvents were dried and distilled using common techniques unless otherwise mentioned. ^{1}H and ^{13}C NMR spectra were recorded at 250.13 and 62.90 MHz respectively on a Brucker AC250 instrument. UV/Vis absorption spectra were recorded on a J&M JIDAS spectrometer. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 solution using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag wire as pseudo reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as an internal reference. Elemental analysis was performed on a Perkin Elmer Analyser 240. Ligands **3**[15] and **4**[18] were prepared according to reported procedures.

Synthesis

1. 4-Isopropyl-phenylazide (322 mg, 2.00 mmol) and 2-ethynylpyridine (206 mg, 2.00 mmol) were dissolved in CH_2Cl_2–*tert*-butanol–H_2O (2.5 : 5 : 2.5 mL). $CuSO_4{\cdot}5H_2O$ (25.0 mg, 0.10 mmol), sodium ascorbate (79.0 mg, 0.40 mmol) and tris-(benzyltriazolylmethyl)amine (11.0 mg, 0.02 mmol) were added and the solution was stirred for 2 d at room temperature. The reaction mixture was poured into water (50 mL) and was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water (20 mL), dried over Na_2SO_4 and the solvent was evaporated. The compound was dried *in vacuo* to give the desired product as a yellow oil. Yield: 500 mg (95%). Found C, 72.97; H, 6.37; N, 20.45% $C_{16}H_{16}N_4$ requires C, 72.70; H, 6.10; N, 21.20%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 1.27 (d, $^3J = 6.9$ Hz, 6H, –CH_3, isopropyl), 2.97 (sept., 1H, –CH, isopropyl), 7.23 (t, $^3J = 6.1$ Hz, 1H), 7.37 (d, $^3J = 8.5$ Hz, 2H), 7.70 (d, $^3J = 8.5$ Hz, 2H), 7.78 (t, $^3J = 7.8$ Hz, 1H), 8.23 (d, $^3J = 7.9$ Hz, 1H), 8.55 (s, 1H, 5-triazole$H$), 8.59 (d, $^3J = 4.4$ Hz, 1H); ^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$): δ/ppm 23.8, 33.8, 119.8, 120.3, 120.4, 122.9, 127.7, 134.9, 136.8, 148.7, 149.4, 149.8, 150.1; HRMS (ESI): Calcd for $C_{16}H_{15}N_4Na$ ([M + Na]$^+$): 287.1267; Found 287.1267.

2. Ligand **2** was synthesised by using a procedure identical to **1** using mesitylazide instead of 4-isopropyl-phenylazide. Yield: 500 mg (95%). Found C, 71.08; H, 6.00; N, 20.87% $C_{16}H_{16}N_4$ requires C, 72.70; H, 6.10; N, 21.20%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 2.02 (s, 6H, *o*-CH_3 groups, mesityl), 2.37 (s, 3H, *p*-CH_3 group, mesityl), 7.01 (s, 2H, phenyl$H$, mesityl), 7.25 (t, $^3J = 6.0$ Hz, 1H), 7.82 (t, $^3J = 7.8$ Hz, 1H), 8.20 (s, 1H, 5-triazole$H$), 8.28 (d, $^3J = 7.9$ Hz, 1H), 8.61 (d, $^3J = 4.0$ Hz, 1H); ^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$): δ/ppm 17.3, 21.1, 120.4, 122.9, 124.0, 129.1, 133.5, 135.0, 136.9, 140.1, 148.2, 149.4, 150.3; HRMS (ESI): Calcd for $C_{16}H_{15}N_4Na$ ([M + Na]$^+$): 287.1267; Found 287.1274. Despite repeated attempts at purification the value of carbon in elemental analyses did not improve. The purity of this substance was ascertained by ^{1}H and ^{13}C NMR spectroscopy (see Fig. S1 and S2†).

1a. Under an argon atmosphere **1** (26.4 mg, 0.10 mmol) and Pd(COD)Cl_2 (28.4 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 1 h and the formed precipitate was collected by filtration. After washing with *n*-hexane (10 mL) the compound was dried *in vacuo* to give the desired product. Yield: 40 mg (90%). Found C, 43.32; H, 3.95; N, 12.52% $C_{16}H_{16}N_4Cl_2Pd$ requires C, 43.51; H, 3.65; N, 12.69%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 1.25 (d, $^3J = 6.8$ Hz, 6H, –CH_3, isopropyl), 2.96 (sept., 1H, –CH, isopropyl), 7.20 (t, $^3J = 6.3$ Hz, 1H), 7.42 (d, $^3J = 8.3$ Hz, 2H), 7.75 (d, $^3J = 8.5$ Hz, 2H), 7.82 (t, $^3J = 7.7$ Hz, 1H), 8.35 (d, $^3J = 7.8$ Hz, 1H), 8.75 (s, 1H, 5-triazole$H$), 9.02 (d, $^3J = 4.6$ Hz, 1H, 6-pyridyl$H$).

2a. Similar to **1a** by using **2** and Pd(COD)Cl_2. Yield: 40 mg (90%). Found C, 43.42; H, 3.93; N, 12.57% $C_{16}H_{16}N_4Cl_2Pd$ requires C, 43.51; H, 3.65; N, 12.69%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 2.02 (s, 6H, *o*-CH_3 groups, mesityl), 2.34 (s, 3H, *p*-CH_3 group, mesityl), 6.99 (s, 2H, phenyl$H$, mesityl), 7.52 (t, $^3J = 6.5$ Hz, 1H), 7.79 (d, $^3J = 7.7$ Hz, 1H), 8.07 (t, $^3J = 6.5$ Hz, 1H),8.21 (s, 1H, 5-triazole$H$), 9.37 (d, $^3J = 4.6$ Hz, 1H, 6-pyridyl$H$).

3a. Similar to **1a** by using **3** and Pd(COD)Cl_2. Yield: 38 mg (95%). Found C, 38.92; H, 2.63; N, 14.27% $C_{13}H_{10}N_4Cl_2Pd$ requires C, 39.08; H, 2.52; N, 14.02%; ^{1}H NMR (250 MHz, dmso-d_6): δ/ppm 7.59–7.65 (m, 5H, phenyl$H$), 7.87 (d, $^3J = 6.5$ Hz, 1H), 8.19 (d, $^3J = 7.6$ Hz, 1H), 8.43 (t, $^3J = 7.7$ Hz, 1H), 9.38 (d, $^3J = 5.4$ Hz, 1H, 6-pyridyl$H$), 9.90 (s, 1H, 5-triazole$H$).

4a. Similar to **1a** by using **4** and $Pd(COD)Cl_2$. Yield: 40 mg (90%). Found C, 39.89; H, 3.33; N, 12.87% $C_{14}H_{12}N_4Cl_2Pd$ requires C, 40.66; H, 2.92; N, 13.55%; ^{1}H NMR (250 MHz, dmso-d_6): δ/ppm 5.78 (s, 2H, $-CH_2-$, benzyl), 7.30–7.48 (m, 5H, phenyl*H*, benzyl), 7.62 (dt, ^3J = 6.6 Hz, ^4J = 1.5 Hz, 1H), 8.22 (d, ^3J = 7.7 Hz, 1H), 8.33 (dt, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H), 9.18 (d, ^3J = 5.3 Hz, 1H, 6-pyridyl*H*), 9.28 (s, 1H, 5-triazole*H*).

1b. Ligand **1** (50 mg, 0.19 mmol) and $Pt(dmso)_2Cl_2$ (80.0 mg, 0.19 mmol) were dissolved in nitromethane and refluxed for 5 h. After removing the solvent diethylether was added and the precipitate was filtered. The compound was washed with acetone (10 mL) and was dried *in vacuo* to give the desired product. Yield: 80 mg (80%). Found C, 36.03; H, 3.28; N, 9.93% $C_{16}H_{16}N_4Cl_2Pt$ requires C, 36.24; H, 3.04; N, 10.56%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 1.26 (d, ^3J = 6.6 Hz, 6H, $-CH_3$, isopropyl), 2.97 (sept., 1H, $-CH$, isopropyl), 7.22 (t, ^3J = 6.3 Hz, 1H), 7.40 (d, ^3J = 8.5 Hz, 2H), 7.70 (d, ^3J = 8.3 Hz, 2H), 7.78 (t, ^3J = 7.4 Hz, 1H), 8.30 (d, ^3J = 7.5 Hz, 1H), 8.78 (s, 1H, $^4J_{Pt-H}$ = 11 Hz, 5-triazole*H*), 9.12 (d, ^3J = 4.5 Hz, $^3J_{Pt-H}$ = 32 Hz, 1H, 6-pyridyl*H*).

2b. Similar to **1b** by using **2** and $Pt(dmso)_2Cl_2$. Yield: 75 mg (75%). Found C, 36.66; H, 3.42; N, 10.96% $C_{16}H_{16}N_4Cl_2Pt$ requires C, 36.24; H, 3.04; N, 10.56%; ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm 2.01 (s, 6H, *o*-CH_3 groups, mesityl), 2.33 (s, 3H, *p*-CH_3 group, mesityl), 6.92 (s, 2H, phenyl*H*, mesityl), 7.49 (t, ^3J = 6.6 Hz, 1H), 7.82 (d, ^3J = 7.6 Hz, 1H), 8.12 (t, ^3J = 6.4 Hz, 1H),8.20 (s, 1H, $^4J_{Pt-H}$ = 10 Hz, 5-triazole*H*), 9.42 (d, ^3J = 4.8 Hz, $^3J_{Pt-H}$ = 32 Hz, 1H, 6-pyridyl*H*).

3b. Similar to **1b** by using **3** and $Pt(dmso)_2Cl_2$. Yield: 83.5 mg (90%). Found C, 31.66; H, 1.86; N, 11.75% $C_{13}H_{10}N_4Cl_2Pt$ requires C, 31.98; H, 2.06; N, 11.48%; ^{1}H NMR (250 MHz, dmso-d_6): δ/ppm 7.63–7.78 (m, 5H, phenyl*H*), 7.91 (d, ^3J = 6.6 Hz, 1H), 8.17 (d, ^3J = 7.7 Hz, 1H), 8.40 (t, ^3J = 7.8 Hz, 1H), 9.36 (d, ^3J = 5.1 Hz, $^3J_{Pt-H}$ = 32 Hz, 1H, 6-pyridyl*H*), 9.87 (s, 1H, 5-triazole*H*).

4b. Similar to **1b** by using **4** and $Pt(dmso)_2Cl_2$. Yield: 67 mg (70%). Found C, 32.81; H, 2.48; N, 10.95% $C_{14}H_{12}N_4Cl_2Pt$ requires C, 33.48; H, 2.41; N, 11.16%; ^{1}H NMR (250 MHz, dmso-d_6): δ/ppm 5.82 (s, 2H, $-CH_2-$, benzyl), 7.34–7.53 (m, 5H, phenyl*H*, benzyl), 7.68 (dt, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 1H), 8.19 (d, ^3J = 7.5 Hz, 1H), 8.31 (dt, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1H), 9.20 (s, 1H, $^4J_{Pt-H}$ = 12 Hz, 5-triazole*H*), 9.32 (d, ^3J = 5.4 Hz, $^3J_{Pt-H}$ = 33 Hz, 1H, 6-pyridyl*H*).

Crystallographic details†

X-Ray data collection, structure solution and refinement for all compounds

Ligand **3** was crystallised by slow evaporation of a dichloromethane solution of the compound layered with *n*-hexane at ambient temperatures. Compound **1a** could be crystallised by slow evaporation of a MeOH–dichloromethane solution and compound **3b** by slow evaporation of a nitromethane solution. The intensity data were collected on a Kappa CCD diffractometer[34] (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 173(2) K for **1a** and **3b** and at 100(2) K for **3**. Crystallographic and experimental details for the structures are summarised in Table 1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[35] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms, with the exception of those of **3**, which were found in the ΔF^2 maps an refined isotropically. A MULTISCAN absorption correction was applied for **3b**.[36]

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