

Palladium(II) Complexes of Readily Functionalized Bidentate 2-Pyridyl-1,2,3-triazole “Click” Ligands: A Synthetic, Structural, Spectroscopic, and Computational Study

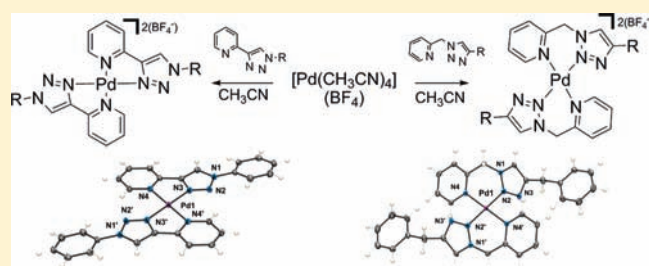
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S Supporting Information

ABSTRACT: The Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes, the CuAAC “click” reaction is currently receiving considerable attention as a mild, modular method for the generation of functionalized ligand scaffolds. Herein we show that mild one-pot “click” methods can be used to readily and rapidly synthesize a family of functionalized bidentate 2-pyridyl-1,2,3-triazole ligands, containing electrochemically, photochemically, and biologically active functional groups in good to excellent yields (47–94%). The new ligands have been fully characterized by elemental analysis, HR-ESI-MS, IR, ¹H and ¹³C NMR and in three cases by X-ray crystallography. Furthermore we have demonstrated that this family of functionalized “click” ligands readily form bis-bidentate Pd(II) complexes. Solution studies, X-ray crystallography, and density functional theory (DFT) calculations indicate that the Pd(II) complexes formed with the 2-(1-R-1H-1,2,3-triazol-4-yl)pyridine series of ligands are more stable than those formed with the [4-R-1H-1,2,3-triazol-1-yl)methyl]pyridine “click” ligands.



INTRODUCTION

Ligand design and synthesis continues to be at the forefront of modern coordination chemistry as it is of crucial importance in many different areas including catalysis,¹ metallo-pharmaceuticals,² bioimaging and sensing,³ metallo-supramolecular chemistry,⁴ and molecular machines.⁵ Despite this there are very few modular, facile, and high yielding methods for the generation of functionalized ligand scaffolds. The recently discovered Cu(I)-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes (the CuAAC reaction)⁶ offers great promise in this regard. This “click” reaction⁷ has quickly become the go-to-reaction for functional molecule synthesis in a wide range of fields, including the biological and materials sciences, because of its reliability, mild reaction conditions, and wide substrate scope.^{6,8} Furthermore, because the 1,4-functionalized 1,2,3-triazoles generated in the CuAAC reaction have the potential to act as either N or C donor ligands there has been an explosion of interest in “click” triazole containing ligand architectures in the past few years.⁹ As such, a range of mono-,¹⁰ bi-,^{11,12} tri-,¹³ and polydentate^{12,14} ligand scaffolds have been created, and their coordination properties with a variety of metal ions examined.

We have recently exploited facile one-pot CuAAC methods for the generation of 1,2,3-triazole¹⁵ and 2-pyridyl-1,2,3-triazole^{16–18} ligands and examined their coordination properties with copper(II), silver(I), palladium(II), platinum(II), gold(I), and gold(III)

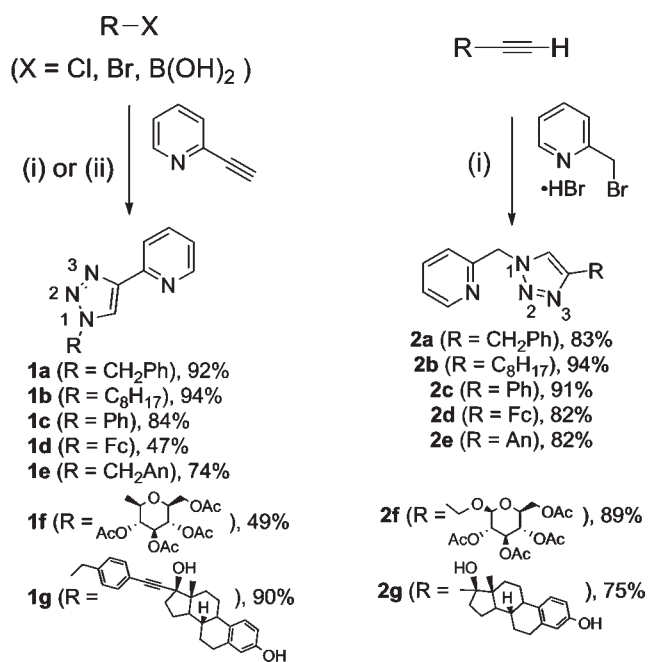
ions. Herein we extend that work and show that the one-pot CuAAC methods can be used to readily and safely incorporate “useful” functional groups onto the 2-pyridyl-1,2,3-triazole scaffold. Furthermore, we examine the coordination chemistry of the resulting ligands with square-planar d⁸ palladium(II) ions, and show that altering the steric or electronic properties of the peripheral substituents has little to no effect on the formation of the bis-bidentate palladium complexes.

RESULTS AND DISCUSSION

Ligand Synthesis and Characterization. We have previously reported the synthesis of the alkyl, benzyl, and phenyl substituted “click” ligands (**1a–c** and **2b–d**) using efficient one-pot CuAAC “click” methodologies.^{15–18} We set out to employ these mild one-pot “click” methods to readily and safely incorporate “useful” functionality into the 2-pyridyl-1,2,3-triazole ligand architectures. As a proof-of-principle, we have been able to readily and rapidly synthesize a small family of functionalized bidentate 2-pyridyl-1,2,3-triazole ligand architectures,¹⁹ containing electrochemically^{17,20–22} (**1d** and **2d**), photochemically²³ (**1e** and **2e**), and biologically^{24,25} (**1fg** and **2fg**) interesting functional groups in good to excellent

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Scheme 1^a

^a (i) NaN₃, CuSO₄·5H₂O, ascorbic acid, Na₂CO₃, DMF/H₂O (4:1), RT or 95 °C, 20 h; (ii) (a) NaN₃, Cu(OAc)₂, MeOH, 55 °C, 2 h, (b) Na ascorbate, RT, 16 h. Isolated yield after chromatography.

yields (49–94%). The 2-pyridyl-1,2,3-triazole ligands (**1a–b**, **1e–g**, and **2a–g**) were synthesized using the standard Fokin²⁶ conditions (Scheme 1 (i)). Simply mixing 2-ethynylpyridine, the appropriate benzyl or alkyl bromide/chloride, NaN₃, CuSO₄·5 H₂O, Na₂CO₃, and ascorbic acid in DMF/H₂O (4:1) then stirring at room temperature for 20 h (Scheme 1) provided, after a simple work up, the desired ligands in good to excellent yields (49–94%) without the need for isolating the potentially hazardous azide intermediates. However, under the standard Fokin conditions only modest yields of the ligands (**1b**, **1e**, and **1f**) were obtained, presumably because the substitution of the halide leaving groups by azide was slow at room temperature. Simply increasing the temperature of the reaction to 95 °C enabled the desired ligands to be generated in moderate to good isolated yields (Scheme 1). We have previously shown that the phenyl substituted ligand (**1c**) could be synthesized by modifying²⁷ the one-pot CuAAC method developed by Liang.²⁸ Disappointingly, when we attempted to generate the ferrocene substituted ligand (**1d**) under these conditions, using iodoferrocene as the starting material, we were only able to recover ferrocene and some unreacted 2-ethynylpyridine from the reaction mixture. Because of this difficulty, we explored alternative methods for the generation of **1c** and **1d** and found that by using a modification²⁹ of the method reported by Guo and coworkers,³⁰ we were able to generate **1c** and **1d** in satisfactory yields. Thus, stirring the appropriate boronic acid, NaN₃, and Cu(OAc)₂ in dry MeOH for 2 h at 55 °C resulted in the in situ generation of the azido intermediate. After cooling to room temperature, sodium ascorbate and 2-ethynylpyridine were added, and the resulting suspension was stirred at room temperature for a further 16 h, yielding the desired aryl/ferrocenyl functionalized ligands in acceptable yields (**1c**, 84%, **1d** 47%), without the need for isolating the potentially hazardous azide intermediates (Scheme 1(ii)).

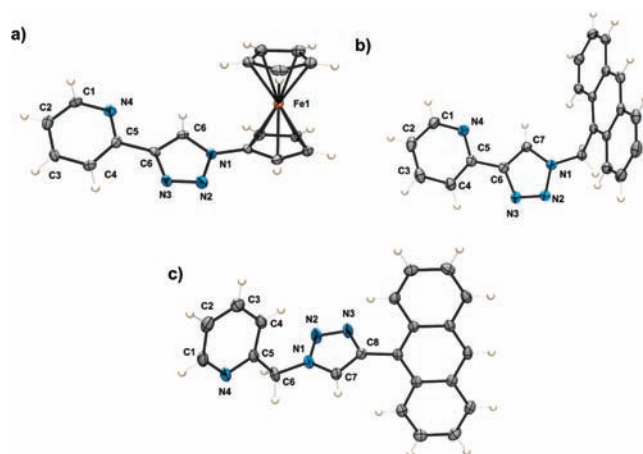


Figure 1. Molecular structures of **1d** (a), **1e** (b), and **2e** (c) are shown as ORTEP diagrams. The thermal ellipsoids are shown at the 50% probability level.

The new ligands **1d–g**, **2a**, and **2e–f** have been fully characterized by elemental analysis, HR-ESI-MS, IR, ¹H and ¹³C NMR spectroscopy. The 2-pyridyl-1,2,3-triazole derivatives were characterized by the lack of an azide (~2095 cm⁻¹) or alkyne (~2150 cm⁻¹) band in their IR spectra and by the diagnostic singlet of the triazole unit (found between 8.6 and 7.5 ppm) in their ¹H NMR spectra (see Supporting Information). Additionally, in the case of the ferrocene (**1d**) and anthracene substituted ligands (**1e** and **2e**), the structures were confirmed by X-ray crystallography (Figure 1, Table 1) and are similar to other structurally characterized 2-pyridyl-1,2,3-triazole ligands.^{17,18,25,31} The ligands in this study all crystallized in the monoclinic space group (either *P2*₁/*c*, **1e**, or *P2*₁/*n*, **1d** and **2e**) with 4 molecules in the unit cell. The ligands **1e** and **1d** are essentially planar with respect to the 2-pyridyl and triazole rings, and as observed in similar structures, the 2-pyridyl substituent is orientated in such a way that electronic repulsion between N(4) of the pyridyl substituent and N(3) of the adjacent triazole is minimized. The ferrocenyl unit of **1d** is rotated by 26° from the triazole ring breaking the planarity of the system. Ligand **2e**, which contains a methylene linker between the pyridyl and the triazole rings, shows similar characteristics with the 2-pyridyl group again positioned to minimize the repulsion between N(4) and N(2). Unlike the 2-pyridyl rings in **1e** and **1d**, the anthracenyl group is not coplanar with the triazole ring but rotated by 73° from the triazole ring.

Synthesis of Pd(II) Complexes. Palladium(II) complexes continue to be of great importance in catalysis,³² metallo-pharmaceuticals,³³ and metallo-supramolecular^{4,34} chemistry and are potentially useful models of the corresponding less-labile platinum(II) complexes. With this in mind we attempted to synthesize and structurally characterize palladium(II) complexes of the 2-pyridyl-1,2,3-triazole ligands.^{16,35–37} The palladium(II) complexes were prepared by adding an acetonitrile solution of [Pd(CH₃CN)₄](BF₄)₂ (1 equiv) to an acetonitrile solution of one of the ligands (**1a–g**, or **2a–g**, 2 equiv) and stirring the resulting reaction mixtures at room temperature for 1 h (Scheme 2). In some cases the palladium complexes precipitated from solution, in others the addition of diethyl ether to the reaction mixtures led to the precipitation of white to pale yellow microcrystalline powders which were isolated by filtration in excellent yields

Table 1. Crystallographic Data for Triazole Ligands and Pd(II) Triazole Complexes

	1d	1e	2e	3a·2CH ₃ CN
CCDC depository	820913	820911	820920	820910
crystallization solvents	CDCl ₃ /pet. ether	CDCl ₃ /Et ₂ O	CH ₂ Cl ₂ /pentane	CH ₃ CN/Et ₂ O
empirical formula	C ₁₇ H ₁₄ N ₄ Fe	C ₂₂ H ₁₆ N ₄	C ₂₂ H ₁₆ N ₄	C ₃₂ H ₃₀ B ₂ N ₁₀ F ₈ Pd
formula weight	330.17	336.39	336.39	834.68
T (K)	91(2)	91(2)	91(2)	91(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> ₂ ₁ / <i>n</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>n</i>	<i>P</i> ₂ ₁ / <i>n</i>
<i>a</i> (Å)	5.8286(16)	10.2602(19)	9.3827(8)	10.232(2)
<i>b</i> (Å)	20.066(5)	9.2476(15)	17.5950(16)	11.358(2)
<i>c</i> (Å)	11.830(3)	17.478(3)	10.9841(10)	14.874(3)
α (deg)	90	90	90	90
β (deg)	92.795(12)	99.840(8)	112.618(4)	96.311(6)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	1382.0(6)	1633.9(5)	1673.9(3)	1718.0(6)
<i>Z</i>	4	4	4	2
ρ _{calc} (mg mm ⁻³)	1.587	1.367	1.335	1.614
μ (mm ⁻¹)	1.092	0.084	0.082	0.625
crystal size (mm)	0.20 × 0.10 × 0.07	0.23 × 0.21 × 0.19	0.36 × 0.25 × 0.12	0.61 × 0.31 × 0.30
color, habit	orange, plate	yellow, block	orange, block	yellow, block
reflections collected	16088	25691	30468	15411
independent reflections (R _{int})	1791 (0.0887)	3334 (0.0622)	3438 (0.0470)	3192 (0.0259)
data/restraints/parameters	1791/0/199	3334/0/236	3438/0/235	3192/0/242
goodness of fit	1.153	1.076	1.059	1.041
final R indexes [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0654 <i>wR</i> ₂ = 0.1715	<i>R</i> ₁ = 0.0513 <i>wR</i> ₂ = 0.1239	<i>R</i> ₁ = 0.0369 <i>wR</i> ₂ = 0.0885	<i>R</i> ₁ = 0.0202 <i>wR</i> ₂ = 0.0487
final R indexes (all data)	<i>R</i> ₁ = 0.0762 <i>wR</i> ₂ = 0.1805	<i>R</i> ₁ = 0.0668 <i>wR</i> ₂ = 0.1326	<i>R</i> ₁ = 0.0524 <i>wR</i> ₂ = 0.0961	<i>R</i> ₁ = 0.0225 <i>wR</i> ₂ = 0.0500
largest diff. peak/hole	1.712 and -0.587	0.230 and -0.216	0.196 and -0.214	0.309 and -0.344
Flack <i>x</i> parameter				

	3c	3d·2CH ₃ CN	3e	4a·2CH ₃ CN
CCDC depository	820912	820907	820917	820915
crystallization solvents	DMSO/CH ₃ OH	CH ₃ CN/Et ₂ O	DMSO/MeOH	CH ₃ CN/Et ₂ O
empirical formula	C ₂₆ H ₂₀ B ₂ N ₈ F ₈ Pd	C ₃₈ H ₃₄ B ₂ N ₁₀ F ₈ Fe ₂ Pd	C ₄₄ H ₃₂ B ₂ N ₈ F ₈ Pd	C ₃₄ H ₃₄ B ₂ N ₁₀ F ₈ Pd
formula weight	724.52	1022.47	952.80	862.73
T (K)	91(2)	91(2)	91(2)	91(2)
crystal system	triclinic	monoclinic	tetragonal	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> ₂ ₁ / <i>c</i>	<i>I</i> ₄ ₁ / <i>a</i>	<i>P</i> ₂ ₁ / <i>n</i>
<i>a</i> (Å)	7.5443(6)	9.659(5)	24.149(4)	11.0379(9)
<i>b</i> (Å)	9.8221(8)	9.496(5)	24.149(4)	10.7240(8)
<i>c</i> (Å)	9.8607(8)	20.364(10)	13.576(5)	15.4582(11)
α (deg)	89.426(4)	90	90	90
β (deg)	68.482(4)	92.834(19)	90	98.057(4)
γ (deg)	77.336(4)	90	90	90
<i>V</i> (Å ³)	661.23(9)	1865.6(16)	7917(3)	1811.7(2)
<i>Z</i>	1	2	8	2
ρ _{calc} (mg mm ⁻³)	1.819	1.820	1.599	1.581
μ (mm ⁻¹)	0.795	1.331	0.553	0.595
crystal size (mm)	0.45 × 0.21 × 0.08	0.17 × 0.15 × 0.04	0.31 × 0.20 × 0.08	0.34 × 0.24 × 0.10
color, habit	yellow, plate	orange, block	yellow, plate	colorless, block
reflections collected	15720	15840	35113	30234
independent reflections (R _{int})	2456 (0.0314)	3284 (0.0809)	4133 (0.0894)	3274 (0.0597)
data/restraints/parameters	2456/0/205	3284/0/307	4133/0/299	3274/0/251
goodness of fit	1.098	1.031	1.072	1.061

Table 1. Continued

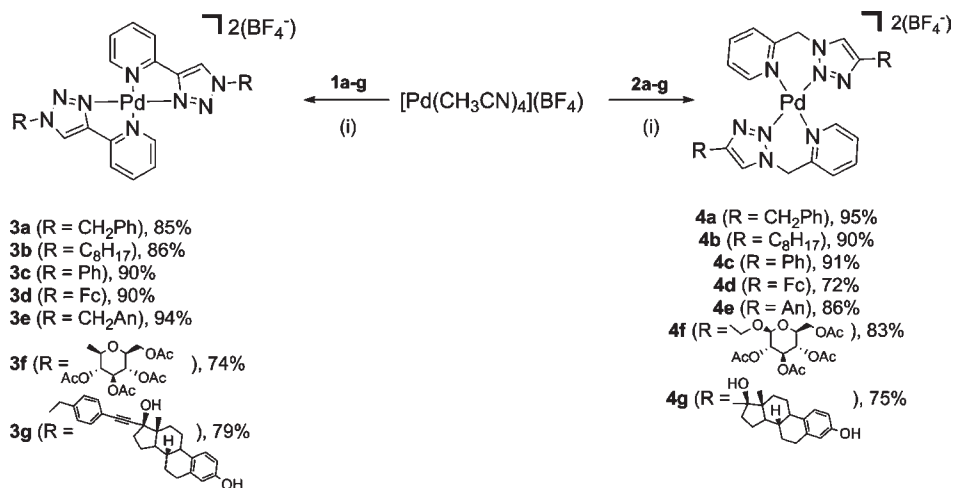
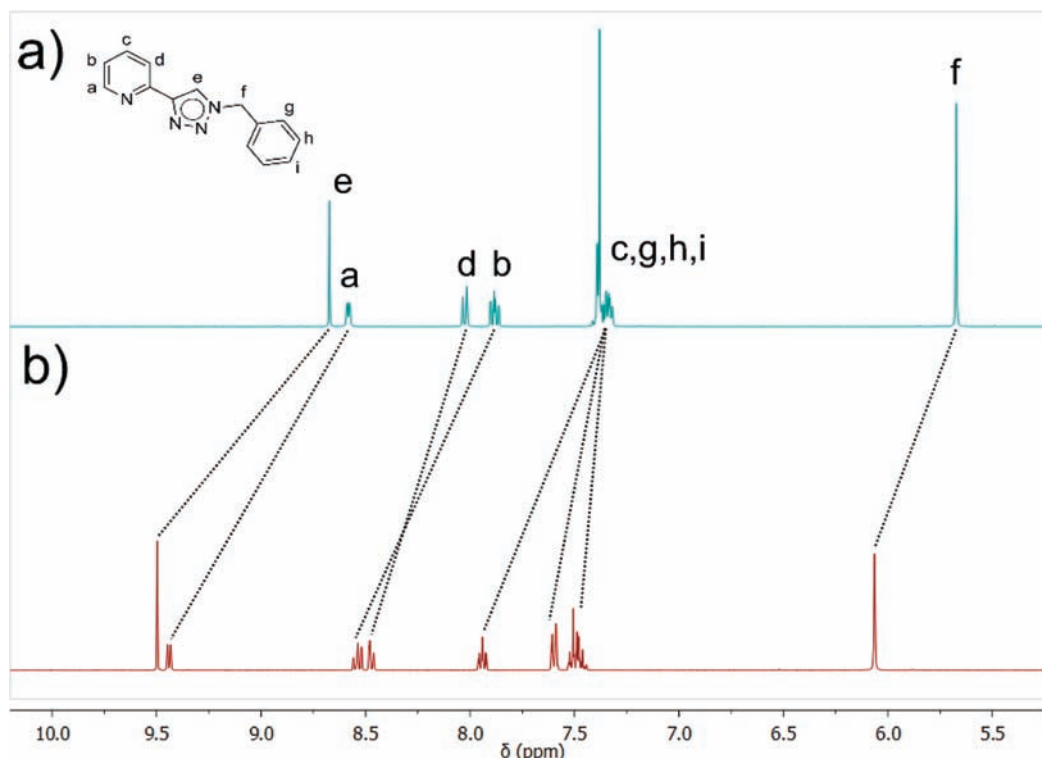
	3c	3d·2CH ₃ CN	3e	4a·2CH ₃ CN	
final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0192 <i>wR</i> ₂ = 0.0463	<i>R</i> ₁ = 0.0460 <i>wR</i> ₂ = 0.1071	<i>R</i> ₁ = 0.0627 <i>wR</i> ₂ = 0.1745	<i>R</i> ₁ = 0.0257 <i>wR</i> ₂ = 0.0600	
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0197 <i>wR</i> ₂ = 0.0466	<i>R</i> ₁ = 0.0719 <i>wR</i> ₂ = 0.1212	<i>R</i> ₁ = 0.0917 <i>wR</i> ₂ = 0.2005	<i>R</i> ₁ = 0.0345 <i>wR</i> ₂ = 0.0635	
largest diff. peak/hole Flack <i>x</i> parameter	0.419 and −0.369	0.635 and −0.460	1.111 and −0.629	0.297 and −0.418	
	4b	4d· ³ / ₄ H ₂ O	4f· ³ / ₂ CH ₃ CN	4g·CH ₃ CN	6a
CCDC depository	820916	820908	820918	820919	820914
crystallization solvents	CH ₃ CN/Et ₂ O	CH ₃ CN/Et ₂ O	CH ₃ CN/Et ₂ O	CH ₃ CN/Et ₂ O	CH ₃ CN/Et ₂ O
empirical formula	C ₃₂ H ₄₈ B ₂ N ₈ F ₈ Pd	C ₃₆ H ₃₂ B ₂ N ₈ O _{0.75} F ₈ Fe ₂ Pd	C ₅₃ H _{66.5} B ₂ N _{11.5} O ₂₀ F ₈ Pd	C ₅₄ H ₆₃ B ₂ N ₉ O ₄ F ₈ Pd	C ₂₆ H ₂₂ B ₂ N ₁₀ F ₈ Pd
formula weight	824.80	980.42	1464.70	1182.15	754.56
<i>T</i> (K)	91(2)	91(2)	91(2)	90(2)	91(2)
crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 1	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.7988(13)	11.138(2)	8.111(3)	14.989(3)	5.2874(5)
<i>b</i> (Å)	9.6946(13)	17.502(3)	8.746(3)	10.953(3)	9.1829(10)
<i>c</i> (Å)	11.9832(17)	20.303(4)	24.179(8)	17.171(4)	15.3551(16)
α (deg)	70.725(7)	76.856(8)	90.852(12)	90	74.415(7)
β (deg)	71.238(7)	86.458(8)	96.818(12)	96.398(9)	86.265(7)
γ (deg)	83.949(7)	77.169(8)	104.357(11)	90	88.227(7)
<i>V</i> (Å ³)	913.6(2)	3757.7(13)	1648.2(9)	2801.5(12)	716.54(13)
<i>Z</i>	1	4	1	2	1
ρ _{calc} (mg mm ^{−3})	1.499	1.733	1.476	1.401	1.749
μ (mm ^{−1})	0.584	1.317	0.383	0.411	0.739
crystal size (mm)	0.36 × 0.32 × 0.09	0.22 × 0.06 × 0.06	0.55 × 0.29 × 0.05	0.28 × 0.12 × 0.06	0.50 × 0.08 × 0.05
color, habit	colorless, block	orange, needle	colorless, plate	colorless, needle	orange, needle
reflections collected	20263	66501	20759	31825	13022
independent reflections (<i>R</i> _{int})	3192(0.0383)	13947 (0.0801)	9985 (0.0640)	10101 (0.0970)	2495 (0.0512)
data/restraints/parameters	3192/0/233	13947/0/1048	9985/9/913	10101/28/733	2495/0/214
goodness of fit	1.087	1.037	1.033	1.024	1.032
final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0265 <i>wR</i> ₂ = 0.0665	<i>R</i> ₁ = 0.0495 <i>wR</i> ₂ = 0.0791	<i>R</i> ₁ = 0.0686 <i>wR</i> ₂ = 0.1601	<i>R</i> ₁ = 0.0732 <i>wR</i> ₂ = 0.1731	<i>R</i> ₁ = 0.0256 <i>wR</i> ₂ = 0.0527
final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0281 <i>wR</i> ₂ = 0.0679	<i>R</i> ₁ = 0.0763 <i>wR</i> ₂ = 0.0884	<i>R</i> ₁ = 0.0832 <i>wR</i> ₂ = 0.1692	<i>R</i> ₁ = 0.1111 <i>wR</i> ₂ = 0.1977	<i>R</i> ₁ = 0.0292 <i>wR</i> ₂ = 0.0543
largest diff. peak/hole Flack <i>x</i> parameter	1.143 and −0.669	0.707 and −0.779	1.927 and −1.623 0.03(3)	0.892 and −0.766 −0.08(4)	0.325 and −0.450

(72–94%). The complexes have been fully characterized by elemental analysis, HR-ESI-MS, IR, ¹H and ¹³C NMR spectroscopy.

Elemental analysis indicated that these bidentate “click” ligands (**1a–g** and **2a–g**) formed palladium(II) complexes with a 1:2 metal/ligand ratio. Consistently, the HR-ESI-MS spectra (acetonitrile or DMF) of the complexes showed major ions due to [(L)₂Pd(BF₄[−])]⁺ and [(L)₂Pd(X = Cl[−] or F[−])]⁺ species. Conductivity measurements in DMF indicated that the palladium(II) complexes (**3a–g** and **4a–g**) behave as 2:1 electrolytes³⁸ with the BF₄[−] anions acting, as expected, as noncoordinating counterions. ¹H NMR spectra of the palladium(II) complexes (**3a–g** and **4a–g**) were recorded at room temperature in *d*₃-acetonitrile or *d*₆-DMSO (see Supporting Information) and in general, the spectra show a simple pattern containing one set of proton signals, suggesting the quantitative formation of single metal containing species. Compared with the spectra of the ligands (**1a–g** and **2a–g**), the proton signals of the corresponding

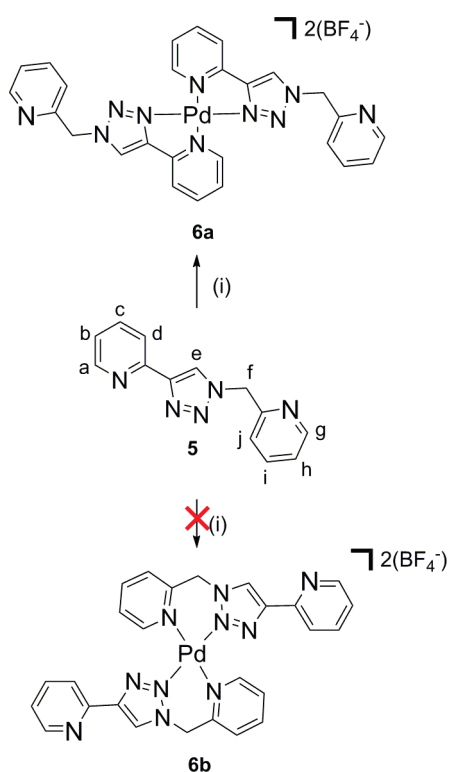
palladium complexes are sharp and shifted downfield indicative of metal complexation in solution (Figure 2 and Supporting Information).

Additionally, we set out to examine experimentally whether the 2-(1-*R*-1*H*-1,2,3-triazol-4-yl)pyridine (**1a–g**) or the [(4-*R*-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**2a–g**) series of ligands form the more stable complexes with Pd(II). Reaction of 2-[1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazol-4-yl]pyridine (**5**)¹⁸ (2 equiv) with [Pd(CH₃CN)₄](BF₄)₂ (1 equiv) in an acetonitrile solution led to the isolation of a palladium(II) complex of the formulation [Pd(**5**)₂](BF₄)₂ as evidenced by HR-ESI-MS and elemental analysis (Scheme 3). Careful examination of the ¹H NMR, COSY and NOESY spectra (*d*₆-DMSO, 298 K) of the ligand **5** and of the palladium(II) complex (either **6a** or **6b**) indicated that the palladium(II) ion was coordinated in the 2-(1*H*-1,2,3-triazol-4-yl)pyridine chelate pocket, suggesting that the complex **6a** is formed under these reaction conditions (Supporting

Scheme 2. Synthesis of the Palladium(II) Complexes^a^a (i) CH₃CN, RT, 1 h.Figure 2. Partial ¹H NMR spectra (400 MHz, *d*₆-DMSO, 298 K, 2 mM) of (a) the ligand **1a**, and (b) the palladium(II) complex **3a**.

Information, Figure S1). This was confirmed unequivocally by X-ray crystallography (vide infra, Figure 4e). Having determined that the 5-membered chelate pocket is more stable in this intramolecular competition experiment, we further examined the stability of the palladium(II) complexes formed with the 2-(1-*R*-1*H*-1,2,3-triazol-4-yl)pyridine (**1a–g**) and [(4-*R*-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**2a–g**) series of ligands using intermolecular competition experiments. [Pd(CH₃CN)₄](BF₄)₂ (1 equiv), **1a** (2 equiv), and either **2a** or **2c** (2 equiv) were dissolved into *d*₆-DMSO and stirred at room temperature for 30 min. ¹H NMR spectroscopy (*d*₆-DMSO, 298 K) of the resulting reaction mixtures

indicated the exclusive formation of the palladium complex **3a** with the corresponding [(4-*R*-1*H*-1,2,3-triazol-1-yl)methyl]pyridine ligand (either **2a** or **2c**) uncomplexed in solution. (Supporting Information, Figures S2–S3). In a second series of competition experiments the ligand **1a** (2 equiv) and the palladium complex (either **4a** or **4c** (1 equiv)) were dissolved into *d*₆-DMSO and stirred at room temperature for 30 min. Once again ¹H NMR spectroscopy (*d*₆-DMSO, 298 K) of the resulting reaction mixtures indicated the exclusive formation of the palladium complex **3a** (Supporting Information, Figures S4–S5). Consistently, the HR-ESI-MS spectra (acetonitrile/*d*₆-DMSO) of the

Scheme 3. Attempted Synthesis of the Palladium(II) Complexes 6a and 6b^a

^a (i) $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, CH_3CN , RT, 1 h.

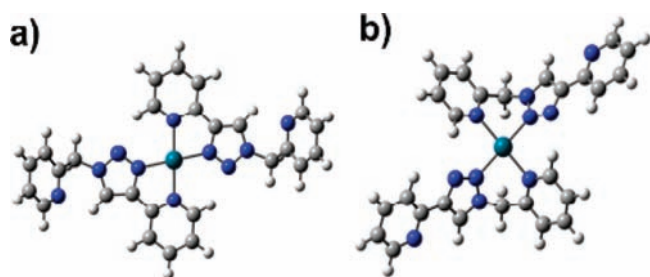


Figure 3. Energy minimized structures of 6a (a) and 6b (b) obtained from DFT calculations (B3LYP and CAM-B3LYP). The calculations indicate that 6a is 83.71 (81.91) kJ mol^{-1} more stable than 6b.

reaction mixture containing Pd(II) ions and the ligands 1a and 2c showed major peaks due to the species $[(1a)_2\text{Pd}(\text{BF}_4^-)]^+$, $[(1a)\text{Pd}(\text{DMSO})_2(\text{HCOOH})(\text{F}^-)]^+$, $[(2c)\text{K}]^+$, and a small peak for $[(1a)\text{K}]^+$. No ions corresponding to the palladium complex 4c could be detected. These results are consistent with expectation, as it is well established that 5-membered chelates, as in complexes 3a–f, are much more stable than 6-membered chelates (4a–f). Second, 3a–f and 6a are coordinated to the metal center through N3 of the triazole ring whereas 4a–f and 6b are coordinated through N2. Density functional theory (DFT) calculations³⁹ have shown that electron density is higher at N3 than at N2; thus, it is not surprising that complexes 3a–f and 6a are more stable than those of 4a–f and 6b. The stability of the palladium complexes was also examined using DFT calculations

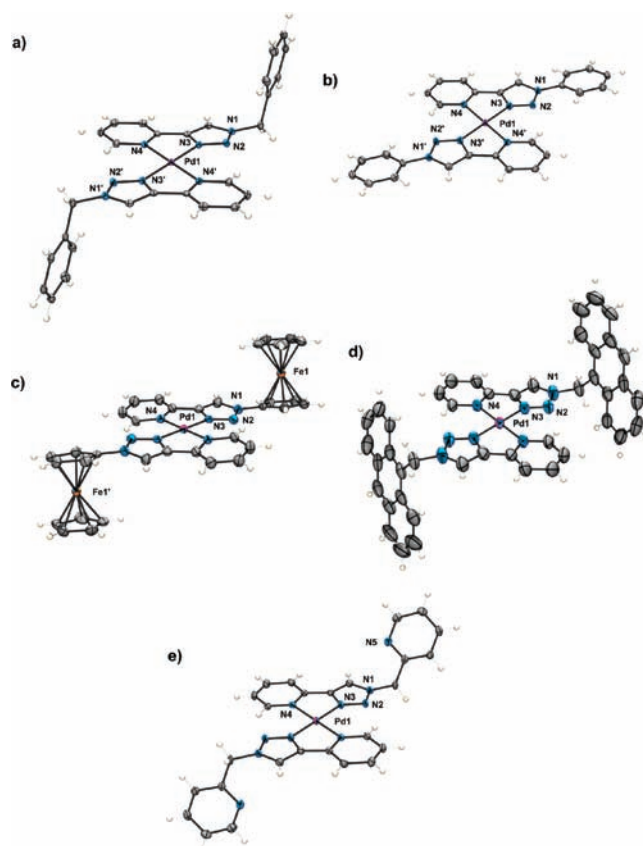


Figure 4. Molecular structures of 3a (a), 3c (b), 3d (c), 3e (d), and 6a (e) are shown as ORTEP diagrams. The thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg) for the complexes are shown in Table 2. Symmetry transformations used to generate equivalent atoms: 3a $-x, -y, -z+2$; 3c $-x+1, -y+1, -z+1$; 3d $-x, -y, -z$; 3e $-x+1, -y, -z+1$; $y+3/4, x-1/4, -z+3/4$; $y+1/4, -x+3/4, -z+3/4$; $-x+1, -y+1/2, z+0$; 6a $-x, -y, -z$.

(B3LYP and CAM-B3LYP, Supporting Information). Consistent with the experimental results, the DFT calculations indicate that 6a is 83.71 kJ mol^{-1} more stable than 6b (Figure 3), and that 3a is 84.47 kJ mol^{-1} more stable than the isomeric complex 4c (Supporting Information, Figure S6).

The molecular structures of the palladium(II) 2-pyridyl-1,2,3-triazole complexes 3a, 3c, 3d, 3e, 4a, 4b, 4d, 4f, 4g, and 6a (Figures 4 and 5, Table 1) were unambiguously confirmed by X-ray crystallography. As expected, two triazole ligands are coordinated to the palladium(II) center in a square-planar fashion via the 2-pyridyl nitrogen and either N2 (4a, 4b, 4d, 4f, and 4g) or N3 (3a, 3c, 3d, 3e, and 6a) of the triazole ring. The divalent charge on the palladium center is balanced by the presence of two noncoordinating BF_4^- anions.

The Pd(II) complexes derived from 2-(1-R-1H-1,2,3-triazol-4-yl)pyridine family of ligands crystallize in either triclinic ($P\bar{1}$, 3c and 6a), monoclinic ($P2_1/n$ 3a, $P2_1/c$ 3d) or tetragonal ($I4_1/a$ 3e) space groups with the Pd positioned on a crystallographic inversion center. Coordination of the ligand gives rise to a 5-membered chelate with the ligands adopting a head-to-tail arrangement around the Pd(II) ions. This arrangement places the peripheral substituents as far apart as possible thereby avoiding any unfavorable steric interactions. Additionally, this orientation of the ligands appears to be further stabilized by a hydrogen bonding

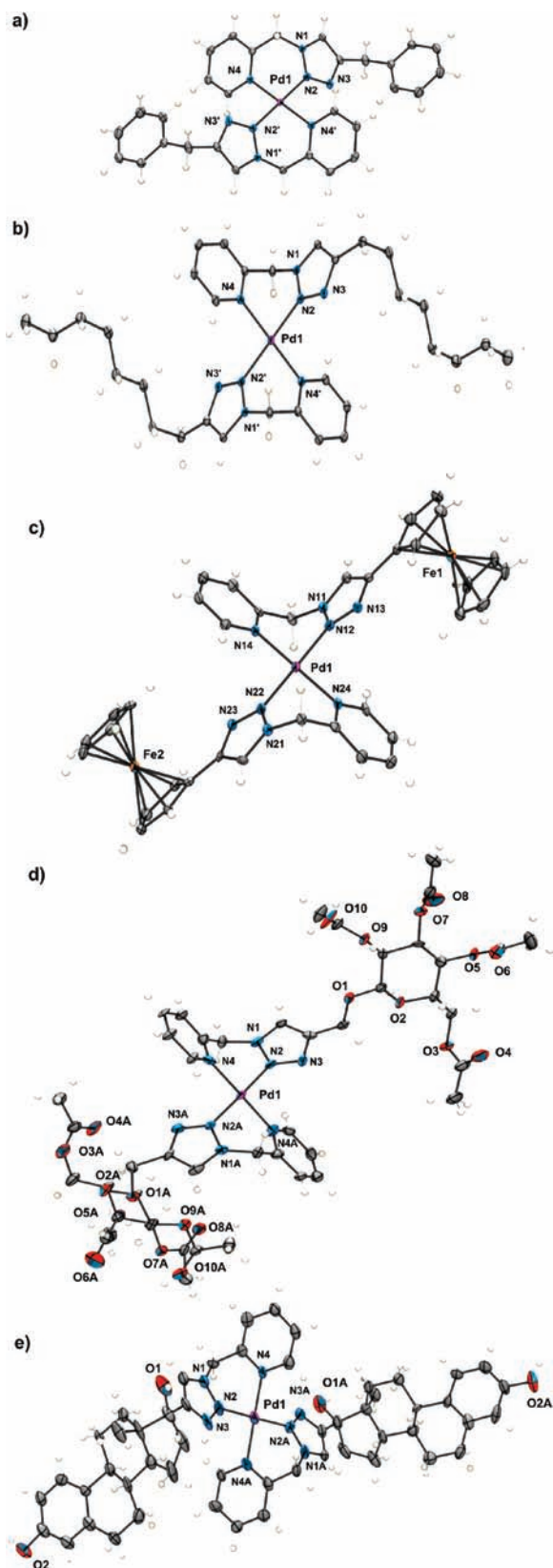


Figure 5. Molecular structures of **4a** (a), **4b** (b), **4d** (c), **4f** (d), and **4g** (e) are shown as ORTEP diagrams. The thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg) are shown in Table 2. Symmetry transformations used to generate equivalent atoms: **4a** $-x+1, -y+1, -z$; **4b** $-x, -y+2, -z+2$; **4d** $-x, -y, -z+1$; $-x+1, -y+2, -z$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of the Palladium(II) Complexes

	$N_{py}-Pd$ (Å)	$N_{trz}-Pd$ (Å)	$N_{py}-Pd-N_{trz}$ (deg)
3a	2.045(1)	1.995(1)	75.59(5)
3c	2.045(2)	2.006(1)	79.56(6)
3d	2.008(4)	1.983(4)	79.54(2)
3e	2.014(4)	1.984(4)	79.81(2)
6a	2.050(2)	1.998(2)	79.93(7)
4a	2.0324(18)	1.9819(18)	87.88(7)
4b	2.0300(17)	1.9909(17)	88.20(7)
4c ^{37,41}	2.037(3)	2.000(3)	88.41(11)
4d	2.038(4), 2.034(4), 2.027(4), 2.035(4)	1.985(4), 1.998(4), 1.988(4), 1.994(4)	86.89(14), 87.81(14), 87.58(16), 88.21(16)
4f	2.024(7), 2.037(7)	2.019(7), 1.993(8)	87.9(3), 87.7(3)
4g	2.044(7), 2.006(7)	1.967(6), 1.984(6)	88.6(3), 87.4(3)

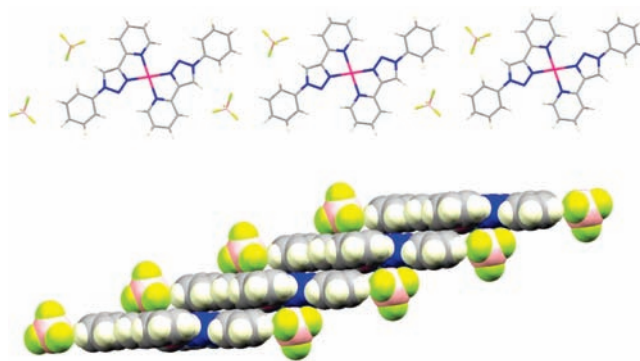


Figure 6. (a) Top view (stick-model) of the planar layers of **3c** showing alternating rows of cations and anions and (b) side view (space-filling model) of **3c**, showing the slip-stacked π -interactions between layers. Color scheme: Gray = carbon, blue = nitrogen, magenta = palladium, pink = boron, green = fluorine.

interaction between the acidic C–H in the 2-position of the pyridyl ring and the N2 nitrogen of the 1,2,3-triazole unit on the adjacent ligand.⁴⁰ In all examples, the core of the molecule (consisting of the Pd(II) center, two triazole and two pyridyl rings) is essentially planar. In the examples **3c** and **3e**, which have either a phenyl or ferrocenyl substituent at N1 of the triazole ring, the planarity extends throughout the molecule. In all the other examples, the pendant substituent is linked to the central triazole ring by a methylene spacer and is therefore able to sit above (and by symmetry below) this planar central core (Supporting Information, Figure S7). From the series of structures characterized, it appears that changing the substituent at N1 of the triazole ring has little influence on the geometry of the palladium complexes, the bite angle of the ligand remains consistent [range 79.54(2)–79.93(7)°] throughout the series, as does the $N_{trz}-Pd$ bond length (Table 2). In addition, the $N_{py}-Pd$ bonds [2.008(4)–2.050(2) Å] are consistently longer than the $N_{trz}-Pd$ bonds [1.983(4)–2.006(1) Å] suggesting the triazolium nitrogens coordinate more strongly to the Pd center than the pyridyl nitrogens of the ligands.

As mentioned above, the cationic moiety of **3c** is essentially planar (Figure 6) and as such crystallizes in a “graphite-like” arrangement with planar sheets layered on top of each other. Each sheet consists of alternating rows of Pd-triazole cations and

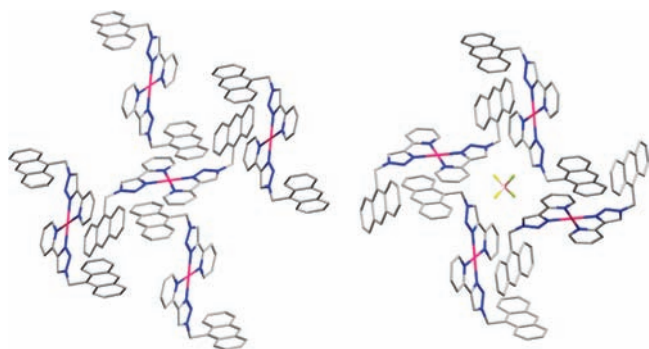


Figure 7. Molecular structures of the complex **3e** showing (a) the planar palladium coordination sphere sandwiched between 2 anthracene substituents and (b) the elongated cavity formed by the arrangement of 4 cationic moieties. Color scheme: Gray = carbon, blue = nitrogen, magenta = palladium, pink = boron, green = fluorine, hydrogen atoms omitted for clarity.

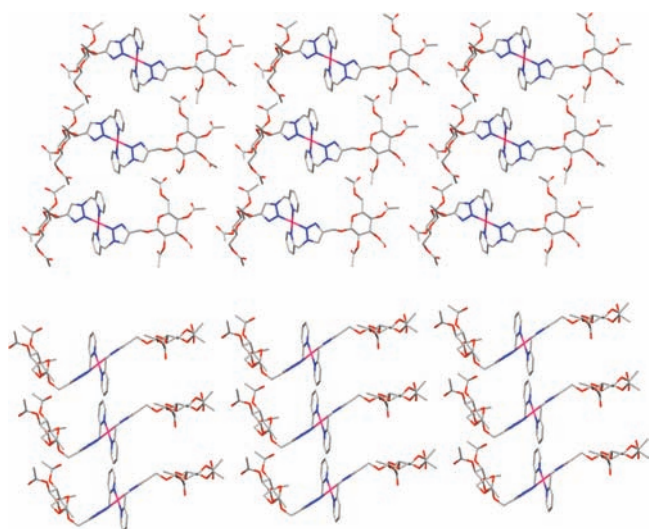


Figure 8. Molecular structures showing (a) rows and (b) columns of cationic moiety of **4f** · 3.5/CH₃CN. Color scheme: Gray = carbon, blue = nitrogen, magenta = palladium, red = oxygen, hydrogen atoms, BF₄[−] anions, and CH₃CN solvent omitted for clarity.

BF₄[−] anions (Figure 6). The sheets are layered on top of each other, with slip-stacked π -interactions being the primary attractive interaction between the layers. The layers are arranged so that the pyridyl ring of the complex interacts with the phenyl ring in the layer above and below, with the average interlayer distance being 3.45 Å.

As expected, when the planarity of the system is broken, the packing arrangement changes drastically. The pendant anthracenyl group of **3e** leads to interesting π - π and π -cation interactions (Figure 7). The planar core of each molecule, consisting of the palladium coordination sphere, is sandwiched between two anthracene groups from different molecules with the average Pd²⁺-anthracene centroid distance of 3.5 Å. In addition, the pendant anthracene substituent bends around to form a face-to-edge interaction (2.579 Å) with one of the sandwiching anthracene moieties. The combination of 4 of the cationic units in this manner

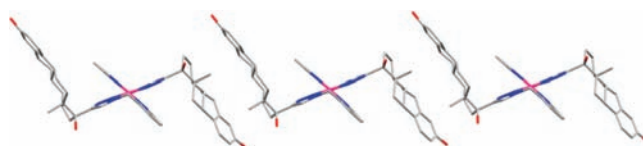


Figure 9. Molecular structures showing the columns of cationic moiety of **4g** · CH₃CN. Color scheme: Gray = carbon, blue = nitrogen, magenta = palladium, red = oxygen, hydrogen atoms, BF₄[−] anions, and CH₃CN solvent omitted for clarity.

Table 3. Comparison of Selected Bond Lengths (Å) of “free” and Pd Coordinated Ligands

	1d	3d	1e	3e
N(3)–N(2)	1.315(8)	1.299(5)	1.318(2)	1.304(6)
N(2)–N(1)	1.345(7)	1.316(5)	1.354(2)	1.324(7)
N(1)–C(7)	1.359(8)	1.340(6)	1.344(2)	1.316(8)
C(6)–C(7)	1.366(9)	1.351(7)	1.370(2)	1.355(8)
N(3)–C(6)	1.362(8)	1.338(6)	1.365(2)	1.349(7)
C(5)–C(6)	1.482(9)	1.430(6)	1.469(2)	1.438(8)

leads to the formation of an elongated supramolecular cage which encapsulates the (disordered) BF₄[−] anions.

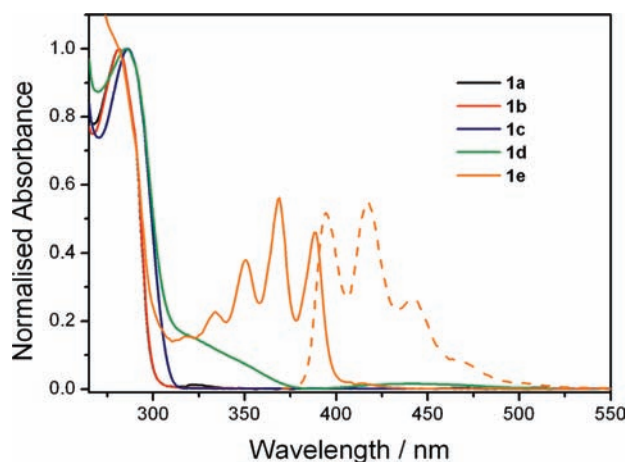
The Pd(II) complexes formed with the [(4-*R*-1*H*-1,2,3-triazol-1-yl)methyl]pyridine series of ligands, crystallized in either triclinic (*P*1 **4f**, *P*1̄, **4b**, **4d**) or monoclinic (*P*2₁/*n* **4a**; *P*2₁ **4g**) space groups. As with the series discussed above, the two ligands also coordinate to the Pd(II) center in a head to tail arrangement, which again places peripheral substituents as far apart as possible (Figure 5 and Supporting Information, Figure S7). However, the presence of the additional methylene spacer between the triazole and the pyridyl groups leads to a less constrained 6-membered chelate and a wider bite angle of the ligand [range 86.95(1)–87.7(3)°]. The 6-membered rings formed by chelation of the ligand adopt boat conformations with the fold angles between the pyridyl and the triazole rings ranging from 109.2–123.57°. As observed with the family of 5-membered systems, altering the substituent on the triazole ring has little effect on the geometry around the Pd center. Interestingly, the Pd–N_{trz} bond lengths remain consistent throughout the entire series of both 5- and 6-membered complexes studied, regardless of whether the triazole is coordinated to the Pd center through N2 or N3. This is somewhat surprising as it has previously been shown by theoretical calculations that N3 is a stronger donor than N2, and in addition the formation of **6a** is favored over **6b** (Scheme 3).

The packing arrangements of structures **4f** and **4g**, which contain pendant glucose and estradiol moieties respectively, have similar arrangements (Figures 8 and 9). Both stack in such a way that their pendant hydrophilic groups interact with the corresponding functionality on a neighboring molecule in effect giving channels of relatively hydrophobic (triazole and pyridyl rings) and hydrophilic regions. Intermolecular interactions are aided by the presence of CH₃CN solvent molecules.

As we were able to obtain X-ray crystal structures of both **1d** and **1e**, and have recently reported the structure of **2d**,¹⁷ a direct comparison of the changes in ligand geometry upon coordination to the Pd(II) cation can be made by examining the parameters of the corresponding complexes **3d**, **3e**, and **4d** (Tables 3 and 4). We were surprised to find that coordination to the metal center had

Table 4. Comparison of Selected Bond Lengths (Å) of “free” and Pd Coordinated Ligands

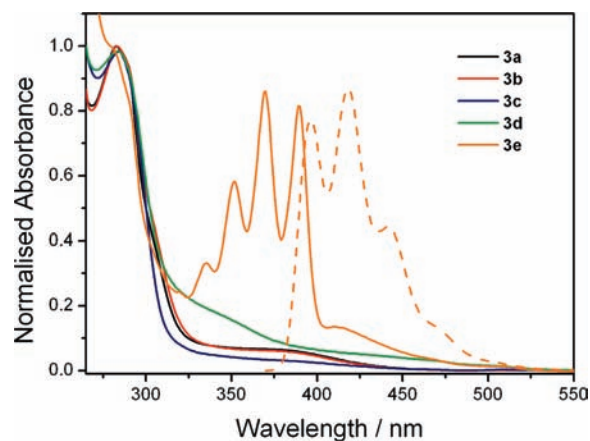
	2d ¹⁷	4d
N(1)–N(2)	1.345(2)	1.336(5), 1.342(5), 1.340(5), 1.344(5)
N(2)–N(3)	1.317(2)	1.330(5), 1.320(5), 1.320(5), 1.320(5)
N(3)–C(8)	1.362(2)	1.355(5), 1.354(5), 1.355(6), 1.351(6)
C(7)–C(8)	1.373(2)	1.380(6), 1.387(6), 1.384(6), 1.388(6)
N(1)–C(7)	1.347(2)	1.341(5), 1.333(5), 1.337(6), 1.335(6)

**Figure 10.** Electronic absorption spectra of **1a–e** (solid lines) and emission of **1e** (dashed line) in DMF. Spectra have been normalized to the highest intensity transition.

little effect on the geometry of the ligand, only very slight decreases in all the bond lengths of the ligands were observed upon complexation.

Photophysical Properties and DFT Calculations. Electronic absorption spectra of the “click” ligands (**1a–f** and **2a–f**) and the palladium complexes (**3a–f** and **4a–f**) were acquired in dimethylformamide (DMF) solution because of the modest solubility of some of the complexes in other common solvents. The spectra of **1a–e** and **3a–e** are displayed in Figures 10 and 11, respectively. The high energy absorption maximum of **2a–f** and **4a–f** were found to overlap quite strongly with the solvent cutoff region of DMF and consequently little can be inferred about their electronic properties and as such they will not be discussed further. However, the compounds that exhibit bands in the visible region (**2d,e** and **4d,e**) mimic the behavior of their **1** and **3** analogues.

Ligands **1a–e** show a distinct transition centered around 280 nm for all compounds, the consistency in the appearance of this band indicates that it arises from a $\pi-\pi^*$ transition localized across the ligand backbone. There is a slight redshift in this transition from 281 nm for **1a–b,e** to 285 nm for **1c**. This likely arises from the extension of the π backbone of the ligand through the substitution of a phenyl at the N1 position. This extended conjugation is not observed for **1e** because of the insulating effect of the methylene between the ligand core and the pendant anthracenyl moiety. **1d** also shows a slight red shift of the ligand $\pi-\pi^*$, but the wavelength and intensity of the ferrocenyl band suggest the spectrum is a superposition of independent pyridyl-1,2,3-triazole ligand $\pi-\pi^*$ and metal-centered (ferrocene-like) transitions. Similarly, the insulated anthracenyl group in **1e** displays

**Figure 11.** Electronic absorption spectra of **3a–e** (solid lines) and emission of **3e** (dashed line) in DMF. Spectra have been normalized to the highest intensity transition.**Table 5.** Electrochemical Data for the Ferrocenyl 1,2,3-Triazole Compounds **1d–4d**

compound	E°/V^a	E_{pc}/V^b
1d	0.78 (CH ₂ Cl ₂)	
	0.71 (CH ₃ CN)	
2d	0.58 (CH ₂ Cl ₂)	
	0.55 (CH ₃ CN)	
3d	0.87 (CH ₃ CN)	–0.30
4d	0.66 (CH ₃ CN)	–0.23

^a Ferrocenyl oxidation (1×10^{-3} M solution; 0.1 M Bu₄NPF₆; GCE; [Fc*]⁺⁰ = 0.00 V). ^b Irreversible reduction (E_{pc} at 100 mVs⁻¹).

the characteristic vibronic structure in the electronic absorption (and emission) with no deviation in the energy of the transitions.

The corresponding palladium complexes **3a–e** display spectra largely identical to that observed for the free-ligand species. There is the appearance of an additional weak band at ~ 375 nm, particularly noticeable in the spectrum of **3a** and **3b**, which shifts to 430 nm in **3e**. The existence of this transition is unclear in the other complexes because of additional conflicting features. In an effort to better understand the electronic structure of these systems DFT calculations were carried out. As a first step, a palladium(II) complex with an unsubstituted triazole ligand was calculated (a detailed method can be found in the Supporting Information). Results from time-dependent DFT calculations (which predict the electronic spectra) show the appearance of a strong series of bands at ~ 286 nm and an extremely weak transition at 370 nm which are $\pi-\pi^*$ and ligand to metal charge-transfer (LMCT) in nature (Supporting Information, Table S2). This leads us to assign the weak transition centered at ~ 375 nm to be of LMCT character. The ability to construct a wide variety of electronically distinct 2-pyridyl-1,2,3-triazole ligands and metal complexes has not been lost on the authors, and an in depth study of their electronic properties will be the subject of a future publication.

Electrochemistry. The electrochemistry of the ferrocenyl species **1d–4d** in dichloromethane and acetonitrile solutions was investigated using cyclic and square wave voltammetric techniques, and the results are presented in Table 5. All show the predicted one-electron chemically reversible ($i_{pc}/i_{pa} \sim 1.0$) oxidation of

the ferrocenyl group (Supporting Information). For the 4-pyridyl-1-ferrocenyl-1,2,3-triazole **1d** E° occurs at 0.78 V (in CH_2Cl_2 solution). This value compares well with that reported previously of 0.74 V for the analogous 4-phenyl-1-ferrocenyl-1,2,3-triazole.⁴² For **2d** the reversible ferrocenyl redox couple appears at 0.58 V. Similar 4-ferrocenyl substituted 1-benzyl- and 1-pentyl-1,2,3-triazoles are oxidized in the range 0.57–0.59 V.^{22,42} Badèche et al. report a value of 0.53 V (in DMSO solution) for both 1-(4-methoxybenzyl)-4-ferrocenyl-1,2,3-triazole and also its derived *trans*- L_2PdCl_2 complex.²¹ For **1d/2d** reduction of the uncoordinated ligand was not observed within the potential window probed. This result is not unexpected as high reduction potentials for 1,2,3-triazole ligands have been observed previously.³⁶

Electrochemistry of the palladium complexes **3d** and **4d** was performed in acetonitrile. In both cases the potential of the ferrocenyl couple is shifted anodically from that of the ligand, concomitant with the decrease in electron density upon coordination to the metal. Additionally, both complexes exhibit an irreversible ligand reduction, with E_{pc} of -0.30 V and -0.23 V for **3d** and **4d**, respectively. The novelty of the compounds makes comparison with other systems difficult, but Schweinfurth et al. report E_{pc} in the range -0.73 to -0.62 V for the irreversible reduction observed in their series of 5-membered $\text{N,N}'$ -chelated LPdCl_2 compounds.³⁶

EXPERIMENTAL SECTION

General Method for the Synthesis of the Pd(II) Complexes.

A solution of tetrakis(acetonitrile)palladium(II) tetrafluoroborate (0.044 g, 0.099 mmol, 1 equiv) in acetonitrile (3 mL) was added to an acetonitrile (3 mL) solution of one of the ligands (**1a–g** or **2a–g**), (0.198 mmol, 2 equiv), and the resulting yellow reaction mixture stirred for 1 h. If the palladium(II) complex precipitated from solution during the course of the reaction, it was isolated by filtration and washed with Et_2O and petrol, then vacuum-dried. If a clear homogeneous solution was obtained after 1 h, the reaction mixture was filtered through a small plug of cotton wool then vapor diffused with diethyl ether to give the complexes as colorless or yellow microcrystalline solids. Full experimental details can be found in the Supporting Information.

X-ray Data Collection and Refinement. X-ray data were recorded using a Bruker APEX II CCD diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by SIR-97.⁴³ Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97⁴⁴ with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. All ORTEP⁴⁵ diagrams have been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1. CCDC 820907–820920 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.

CONCLUSIONS

Using mild one-pot “click” methods we have been able to readily and rapidly synthesize a family of functionalized bidentate 2-pyridyl-1,2,3-triazole ligand architectures, containing electrochemically, photochemically, and biologically active functional groups in good to excellent yields. The new ligands have been fully characterized by elemental analysis, HR-ESI-MS, IR, ^1H and ^{13}C NMR and in three cases by X-ray crystallography. Furthermore we have shown that this family of functionalized “click” ligands readily form bis-bidentate Pd(II) complexes. Solution

studies, X-ray crystallography, and DFT calculations, indicate that the Pd(II) complexes formed with the 2-(1-*R*-1*H*-1,2,3-triazol-4-yl)pyridine series of ligands are more stable than those formed with the [4-*R*-1*H*-1,2,3-triazol-1-yl)methyl]pyridine “click” ligands. Additionally, X-ray crystallography indicates that the formation and stability of the palladium(II) complexes is essentially unaffected by the electronic and steric properties of the “click” ligands’ peripheral substituents. This opens up the possibility of using this family of functionalized bidentate 2-pyridyl-1,2,3-triazoles to generate novel palladium and platinum complexes for use as metallo-pharmaceuticals,⁴⁶ bioimaging devices or catalysts.⁴⁷ Efforts toward these goals are currently underway.

ASSOCIATED CONTENT

Supporting Information. Full experimental descriptions, spectroscopic data, and a CIF file giving crystallographic data for **1d**, **1e**, **2e**, **3a**, **3c**, **3d**, **3e**, **4a**, **4b**, **4d**, **4f**, **4g**, and **6a**. This material is available free of charge via the Internet at <http://pubs.acs.org>. The crystallographic data are also available from the Cambridge Crystallographic Database as file no. CCDC 820907–820920.

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