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Triazoles from N-Alkynylheterocycles and Their Coordination to Iridium

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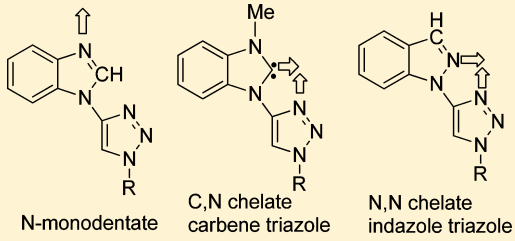
Supporting Information

ABSTRACT: N-alkynylheterocycles (benzimidazole and indazole) are converted to triazoles by click chemistry, and the resulting triazoles react with $[IrCl_2Cp^*]_2$. The benzimidazole-triazole coordinates in a monodentate fashion through the benzimidazole, whereas the indazole-triazole is bidentate through coordination of both heterocycles. Reaction of the benzimidazole-triazole with methyliodide gives a benzimidazolium salt that deprotonates on coordination to afford a rare example of a bidentate NHC−triazole.



INTRODUCTION

Triazoles have received a lot of interest in the past decade due to their easy synthesis by the copper-catalyzed Huisgen [3 + 2] cycloaddition reaction between a terminal alkyne and an azide ("click chemistry"),[1] and this chemistry has been applied in a wide range of fields, including material science, chemical biology, and drug discovery.[2] The application of click chemistry to the synthesis of chelate ligands was first described in 2006 using amino acid derived alkynes or azides.[3] The resultant ligands are bound through a primary amine and either the N(3) or, in some cases, the N(2) of the triazoles (see Figure 1). Since

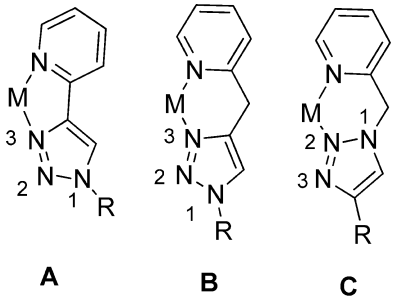


Figure 1. Chelating triazoles derived from 2-ethynyl pyridine (A), 2-picolylethyne (B), and 2-azidomethylpyridine (C).

then, several further examples of this "click-to-chelate" approach have been reported, and the field has been reviewed.[4] The majority of examples use either 2-ethynyl pyridine,[5] which tends to give five-membered chelates of type A (Figure 1), or 2-picolylethyne,[6] which gives six-membered chelates of type B (Figure 1). Both of these ligands coordinate through N(3) as expected, since DFT calculations have shown that N(3) is a better donor than N(2).[3,7] However, coordination through N(2) is also possible using ligands of type C,[8] but the complexes are less stable than those of type A, as has been confirmed experimentally and computationally for a series of palladium complexes.[8c]

The luminescence of pyridine triazoles is sensitive to the presence of metal ions,[9] and the ease of tuning the electronic properties of these ligands has been used to control the luminescence of biscyclometalated iridium complexes.[5d,10] Amido-triazoles have been used in luminescent copper complexes.[11] Recently, chelating triazoles have been applied to the modification of half-sandwich ruthenium complexes to try and improve their anticancer activity.[6]

Perhaps surprisingly, the use of the click-to-chelate approach has not yet been explored greatly for use in homogeneous catalysis, though some phosphine-triazole chelates have been studied.[12] The first example of a chelate formed from an N-heterocyclic carbene and a triazole synthesized via click chemistry was only reported in 2010.[13] In addition, triazoles themselves can also be alkylated and function as precursors to triazolylidenes.[14] We and others have shown that, in the absence of a N or P chelating atom using triazoles derived from phenylalkynes, the triazoles can act as a directing group to facilitate CH activation to form cyclometalated N,C chelates. Thus, triazoles provide a range of opportunities to develop new ligand systems where the electronic and steric properties can be easily tuned by virtue of the types of alkynes and azides utilized.[10c,15]

In all the cases described above, the alkynes used are terminal with one carbon substituent. Azide cycloadditions to ynamides are also known;[16] however, the corresponding reactions with N-alkynyl heterocycles have not been studied. Having recently reported a convenient route to N-alkynyl heterocycles,[17] we decided to test the click reactivity of these and investigate the coordinating ability of the resulting triazoles.

RESULTS AND DISCUSSION

N-alkynylbenzimidazole **1** and N-alkynylindazole **2** were reacted with the appropriate azide in the presence of copper

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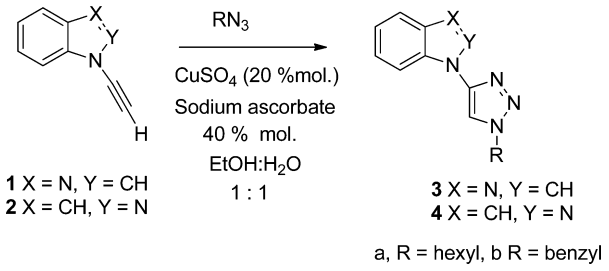
to give triazoles **3** and **4**, respectively (Scheme 1). The click reaction between each N-alkynylheteroarene and the appropriate azide was extremely facile, with the reaction complete in less than 5 min using 20 mol % Cu^{2+} and 40 mol % sodium ascorbate, affording **3** and **4** as white waxy solids in good yield.

Scheme 1. Preparation of Triazoles from N-Alkynylheterocycles



Having synthesized the triazoles, we decided to explore their coordination by reaction with $[IrCl_2Cp^*]_2$. Our previous results have shown that the triazole N(3) can act as a directing group for CH activation of a 4-phenyl group by acetate-assisted cyclometalation with $[IrCl_2Cp^*]_2$.[15a] Additionally, acetate-assisted cyclometalation of heterocycles, such as pyrrole and thiophene, is also known.[18] Hence, synthesis of **6** by cyclometalation of the benzimidazole of **3b** was attempted by reaction with $[IrCl_2Cp^*]_2$ in the presence of sodium acetate (Scheme 2). The ^1H NMR spectrum of the reaction mixture showed the presence of only one Cp*Ir complex (δ 1.66); however, 13 additional proton signals were observed, suggesting that no CH activation had occurred. Three singlets were observed at δ 9.39(1H), 8.01(1H), and 5.31(2H); the latter is clearly due to the benzylic CH_2 group. Moreover, because these protons are equivalent, it suggests that the ligand is not bidentate since this would make the iridium a chiral center, and hence, these protons would be diastereotopic. Hence, the compound is assigned as **5b**. The NOESY spectrum showed a correlation between the singlet at δ 8.01 and a doublet at δ 8.02; hence, this singlet is assigned to the triazole proton. Therefore, the singlet at δ 9.39 is the benzimidazole proton, which is 0.89 ppm downfield from the free ligand, consistent with coordination through the benzimidazole rather than the triazole. This was confirmed by an X-ray structure determination (see Figure 2).

This result suggests that acetate is not required for the reaction, and indeed, if the reaction is repeated omitting the sodium acetate, the same product is formed. A similar reaction with **3a** gives the corresponding hexyl substituted product **5a**. This shows similar features in the ^1H NMR spectrum with the benzimidazole proton being observed at δ 9.35 and the NCH_2 protons being equivalent giving rise to a triplet at δ 4.13. Hence, although coordination through the triazole is feasible, it appears that the benzimidazole is a better donor.

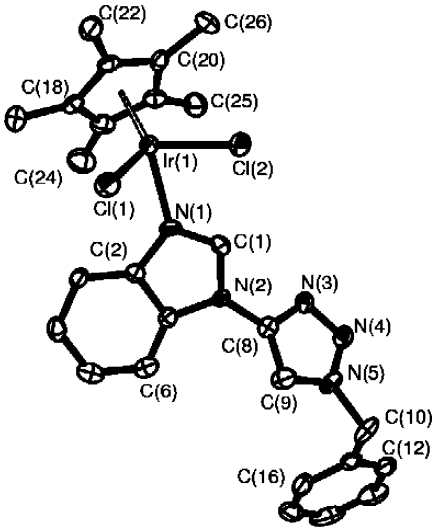
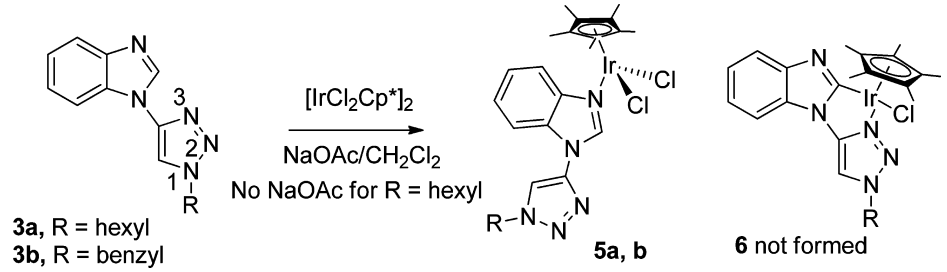


Figure 2. Ortep plot of **5b**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: M−N(1) 2.135(5), M−Cl(1) 2.4191(18), M−Cl(2) 2.4124(18), Ir(1)−C(21) 2.144(7), Ir(1)−C(20) 2.162(7), Ir(1)−C(19) 2.152(6), Ir(1)−C(18) 2.155(7), Ir(1)−C(17) 2.156(7); N(1)−M−Cl(1) 88.52(15), N(1)−M−Cl(2) 85.71(16).

To prevent coordination of the benzimidazole, and to examine the conversion of the ligand to an NHC−triazole chelate, alkylation of **3a** with methyl iodide was attempted. Reaction with methyl iodide proceeded selectively to alkylate the more electron-rich benzimidazole, giving **7a** (Scheme 3); there was no evidence for competing alkylation at the triazole even though this reaction is known.[14c] To our knowledge, this is the first imidazolium directly attached to a triazole. The only previous examples of imidazolium-functionalized triazoles were reported in 2010[13] and have a CH_2 linker between the two heterocycles. Note, in our case, construction of the triazole, followed by alkylation of the benzimidazole, works well; however, in the previous cases, the imidazolium salts had to be made first, followed by cycloaddition to form the triazoles. Even then, click coupling of the imidazolium salts was not very efficient, stoichiometric amounts of copper being required to give good yields.[13] Hence, our procedure provides a novel and facile synthetic method for the preparation of imidazolium-functionalized triazoles.

Scheme 2. Coordination of Triazoles 3a and 3b



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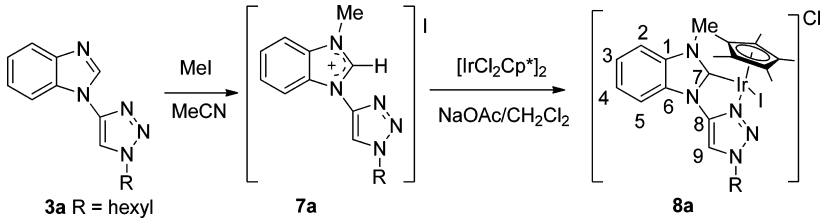
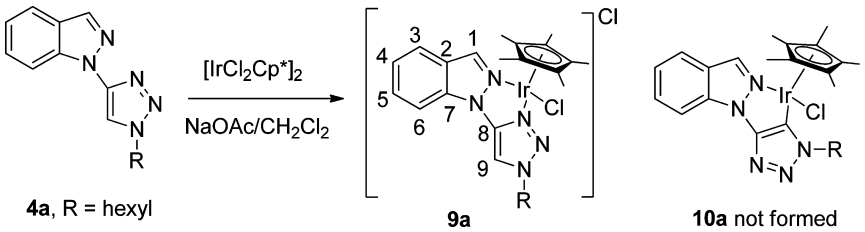
Scheme 3. Preparation of NHC−Triazole Complex 8a and NMR Labeling Scheme



Scheme 4. Coordination of Indazole-Triazole 4a



Subsequently, the benzimidazolium salt **7a** was reacted with $[IrCl_2Cp^*]_2$ in the presence of sodium acetate. After 20 h, the ^{1}H NMR spectrum showed complete reaction, with one set of signals for the ligand and a Cp*, suggesting that the reaction selectively produced one compound. The ^{1}H NMR spectrum of the product showed signals integrating for 38 H (i.e., loss of one H) with only one singlet, at δ 10.94, similar to that of the imidazolium proton H^7 in the free ligand (at δ 10.09). However, in the NOESY spectrum, the singlet at δ 10.94 shows cross peaks with both H^5 and the hexyl chain and hence is assigned as the triazole proton H^9, confirming the loss of H^7 and the formation of carbene complex **8a**. The chemical shift for H^9 in **8a** (δ 10.94, c.f. δ 8.83 in **7a**) is consistent with coordination of the triazole to form a cationic complex with hydrogen bonding of H^9 to the counterion (Cl^-, I^-), causing the low-field NMR shift. The other protons are in typical positions, and NOE correlations between the methyl signal and the Cp* and the methyl and H^2 confirm the assignments. The ^{13}C NMR spectra show the expected number of carbons with the carbene C^7 at δ 173.00, which is slightly deshielded (about 15 ppm) compared with other Cp*Ir NHC complexes.[19] The ES-MS spectrum of **8a** shows one peak at m/z 738, which suggests that iodide is coordinated to the metal with chloride as a counterion. The elemental analysis is also consistent with this formulation.

Next, we examined coordination of indazole-triazole **4a**. In principle, this can act as an N−N chelate; however, if coordination of the indazole occurs first, then subsequent C−H activation of the triazole may also be possible to form **10a** (Scheme 4). The reaction of **4a** with $[IrCl_2Cp^*]_2$ and sodium acetate was carried out, and after 23 h, the ^{1}H NMR spectrum showed one Cp* signal and one set of signals for the ligand integrating to 19 protons, suggesting that no C−H activation had occurred and **10a** was not formed. The ES-MS and FAB-MS showed a peak at m/z 632 assigned as the cation $[IrCl(\mathbf{4a})Cp^*]^+$. Hence, the reaction was repeated without sodium acetate in the presence of KPF_6, to afford **9a** as a PF_6 salt.

The ^{1}H NMR spectrum of **9a** shows two singlets at δ 8.46 and 8.59, which are assigned to H^1 and H^9, respectively. H^9 is 0.7 ppm downfield from the corresponding signal in **4a** (δ 7.85), consistent with coordination of the triazole in a cationic complex making H^9 more acidic. It is not as low field as in **8a** (δ 10.94), possibly reflecting less hydrogen bonding to PF_6 than to chloride in **8a**. The other aromatic protons are observed as two doublets at δ 7.86 (H^6) and 7.88 (H^3) and two doublets of doublets at δ 7.37 (H^4) and 7.66 (H^5). The ^{13}C NMR spectra show the expected number of C−H and quaternary carbons with the imine carbon C^1 at 138.68. The elemental analysis confirmed that the product contains PF_6 as a counterion.

In conclusion, we have shown that N-alkynylbenzimidazole **1** and indazole **2** are easily converted to triazoles **3** and **4**, respectively, by copper-catalyzed addition of azide. The coordination behavior of these triazoles suggests that triazoles are not very strong ligands. Hence, for **1**, coordination via the benzimidazole is preferred; as a result, cyclometalation is not possible. As we observed previously,[15a] in cyclometalation reactions with $[IrCl_2Cp^*]_2$ in the presence of sodium acetate, if a second N or O donor can coordinate to provide a bidentate N,N or N,O ligand, then cyclometalation does not occur. This is the case with the indazole-triazole **4a**, which forms the chelate complex **9a**. Benzimidazole-triazole **3a** is easily methylated (to **7a**), and this reacts with $[IrCl_2Cp^*]_2$ in the presence of sodium acetate to form an NHC−triazole chelate complex **8a**. In contrast to the only previous report on NHC−triazole ligands, in our case, the click reaction can be performed before alkylation; hence, ligands with different substituents can easily be accessed from a common precursor through use of different alkylating agents. In addition, in **7a**, the carbene is directly linked to the triazole rather than with a CH_2 spacer. In conclusion, we have shown than N-alkynyl-derived triazoles can be used to make chelate ligands. Further applications of these ligands in catalysis and in labeling biomolecules are being investigated.

■ EXPERIMENTAL SECTION

All reactions were carried out at room temperature under nitrogen; however, the workup was carried out in air, unless stated otherwise. Solvents were dried by passage through activated alumina and degassed prior to use. ^{1}H, ^{13}C-{^{1}H} NMR spectra were obtained using a Bruker ARX 400 MHz spectrometer, with $CDCl_3$ as a solvent, unless otherwise stated. Chemical shifts were recorded in parts per million (on the δ scale for ^{1}H NMR, with tetramethylsilane as an internal reference), and coupling constants are reported in hertz. FAB mass spectra were obtained on a Kratos concept mass spectrometer

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using NOBA as a matrix, and electrospray (ES) mass spectra were recorded using a micromass Quattro LC mass spectrometer in acetonitrile. Microanalyses were performed by the Elemental Analysis Service (London Metropolitan University). Starting alkynes **1** and **2** were prepared from TIPS-protected alkynes, which were prepared by the literature method.[17] $[IrCl_2Cp^*]_2$,[20] hexyl azide,[21] and benzyl azide[22] were prepared by literature methods; other compounds were obtained from Aldrich and Alfa Aesar.

Preparation of 1. To a solution of 1-((triisopropylsilyl)ethynyl)-1*H*-benzo[*d*]imidazole[17] (0.060 g, 0.200 mmol.) in THF (10 mL) was added a solution of tetrabutylammonium fluoride (1.0 M, 200 μL) at room temperature in air. The reaction was stirred for 30 min, followed by concentration in vacuo in the dark. Column chromatography (10% EtOAc in Petroleum Spirit 40/60) and concentration in vacuo afforded **1** (0.042 g, 74%) as a white crystalline solid. ^{1}H NMR (500 MHz): δ 3.32 (s, 1H, C≡C-*H*), 7.38 (dt, 1H, *J* = 7.9, 0.6 Hz, Ar-*H*), 7.44 (dt, 1H, *J* = 8.2, 1.0 Hz, Ar-*H*), 7.62 (dd, 1H, *J* = 7.9, 0.8 Hz, Ar-*H*), 7.84 (dd, 1H, *J* = 8.2, 0.8 Hz, Ar-H), 8.11 (s, 1H, Ar-*H*). ^{13}C NMR (125.8 MHz): δ 62.1 (C≡*C*-H), 70.3 (*C*≡C−H), 110.9 (Ar-*C*-H), 120.9 (Ar-*C*-H), 124.2 (Ar-*C*-H), 124.9 (Ar-*C*-H), 134.4 (Ar-C_{ipso}), 141.8 (Ar-C_{ipso}), 143.6 (Ar-*C*-H). MS (FAB, +ve mode): calcd for $C_9H_7N_2^+$, 143.06037; found, 143.06079 $[M + H]^+$.

Preparation of 2. This was prepared similarly, starting from 1-((triisopropylsilyl)ethynyl)-1*H*-indazole[17] (0.207 g, 0.695 mmol.). Column chromatography (10% EtOAc in Petroleum Spirit 40/60) and concentration in vacuo afforded **2** (0.096 g, 97%) as a white crystalline solid. ^{1}H NMR (400 MHz): δ 3.47 (s, 1H, C≡C-*H*), 7.29 (dt, 1H, *J* = 7.9, 0.6 Hz, Ar-*H*), 7.52 (dt, 1H, *J* = 7.2, 1.1 Hz, Ar-*H*), 7.61 (dd, 1H, *J* = 8.1, 0.8 Hz, Ar-*H*), 7.74 (dd, 1H, *J* = 8.1, 0.8 Hz, Ar-*H*), 8.11 (s, 1H, Ar-*H*). ^{13}C NMR (125.8 MHz): δ 62.7 (C≡*C*-H), 73.7 (*C*≡C-H), 110.6 (Ar-*C*-H), 121.6 (Ar-*C*-H), 123.4 (Ar-*C*-H), 123.5 (Ar-C_{ipso}), 128.6 (Ar-*C*-H), 138.3 (Ar-*C*-H), 142.4 (Ar-C_{ipso}).

Preparation of 3a. To a solution of 1-ethynyl-1*H*-benzo[*d*]-imidazole **1** (0.390 g, 2.75 mmol) and *n*-hexyl azide (0.699 g, 5.50 mmol) in EtOH (1.0 mL) was added an aqueous solution of $CuSO_4{\cdot}5H_2O$ (0.274 g, 1.10 mmol in 10.0 mL), followed by solid sodium ascorbate (0.436 g, 2.20 mmol) in air. The reaction mixture was stirred at room temperature until complete consumption of **1** (typically 5 min, as monitored by tlc). The reaction mixture was then diluted with ethyl acetate (500 mL) and the organic layer washed with dilute ammonia solution (1%, 1 × 250 mL), followed by brine (2 × 250 mL) and finally water (1 × 250 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (flash SiO_2, EtOAc/hexane 1:1) afforded the desired compound **3a** as a white solid (0.512 g, 80%). ^{1}H NMR (500 MHz): 0.91 (t, 3H, *J* = 7.5 Hz, Me), 1.37 (m, 6H, 3 × CH_2), 2.01 (m, 2H, NCH_2CH_2), 4.47 (t, 2H, *J* = 7.5 Hz, NCH_2), 7.37 (m, 2H, 2 × CH_{bi}), 7.69 (d, 1H, *J* = 7.5 Hz, CH_{bi}), 7.83 (s, 1H, CH_{tr}), 7.88 (d, 1H, *J* = 7.5 Hz, CH_{bi}), 8.38 (s, 1H, NCHN). ^{13}CNMR (125.7 MHz): 13.9 (Me), 22.4, 26.1, 30.2, 31.1 (4 × CH_2), 51.4 (NCH_2), 111.0 (CH_{tr}), 113.8, 120.7, 123.3, 124.2 (4 × CH_{bi}), 132.6 (*C*-*ipso*), 141.3 (NCHN), 142.3 (*C*-*ipso*), 143.8 (*C*-*ipso*). HR-MS (FAB +ve mode): calculated for $C_{15}H_{19}N_5^+$, 269.16405; found, 269.16367 $[M]^+$.

Preparation of 3b. To a solution of 1-ethynyl-1*H*-benzo[*d*]-imidazole **1** (0.031 g, 218 μmol) and benzyl azide (0.035 g, 262 μmol) in EtOH (1.0 mL) was added an aqueous solution of $CuSO_4{\cdot}5H_2O$ (0.011 g, 44 μmol in 1.0 mL), followed by solid sodium ascorbate (0.017 g, 87 μmol) in air. The reaction mixture was stirred at room temperature until complete consumption of **1** (typically 5 min, as monitored by tlc). The reaction mixture was then diluted with ethyl acetate (250 mL) and the organic layer washed with dilute ammonia solution (1%, 1 × 100 mL), followed by brine (2 × 100 mL) and finally water (1 × 100 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (flash SiO_2, EtOAc/hexane 1:1) afforded the desired compound **3b** as a white solid (0.037 g, 61%). ^{1}H NMR (500 MHz): 5.65 (s, 2H, CH_2), 7.36 (m, 4H, Ph), 7.45 (m, 3H, Ph), 7.66 (m, 1H, CH_{bi}), 7.72 (s, 1H, CH_{tr}), 7.87 (m, 1H, CH_{bi}), 8.36 (s, 1H, NCHN). ^{13}C NMR ($CDCl_3$, 125.7 MHz): 55.20 (CH_2), 111.00 (CH), 113.7 (CH), 120.7 (CH), 123.3 (CH), 124.3 (CH), 128.2 (2CH), 129.2 (CH), 129.4 (2CH), 132.5 (*C*-*ipso*), 133.8 (*C*-*ipso*), 141.2 (CH), 142.7 (*C*-*ipso*), 143.8 (*C*-*ipso*). HR-MS (FAB): calculated for $C_{16}H_{14}N_5^+$, 276.12437; found, 276.12454

Preparation of 4a. To a solution of 1-ethynyl-1*H*-indazole **2** (0.062 g, 434 μmol) and *n*-hexyl azide (0.110 g, 867 μmol) in EtOH (2.0 mL) was added an aqueous solution of $CuSO_4{\cdot}5H_2O$ (0.011 g, 43 μmol in 2.0 mL), followed by solid sodium ascorbate (0.017 g, 88 μmol) in air. The reaction mixture was stirred at room temperature until complete consumption of **2** (typically 5 min, as monitored by tlc). The reaction mixture was then diluted with ethyl acetate (250 mL) and the organic layer washed with dilute ammonia solution (1%, 1 × 100 mL), followed by brine (2 × 100 mL) and finally water (1 × 100 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (flash SiO_2, EtOAc/hexane 1:1) afforded the desired compound **4a** as a white solid (0.098 g, 84%). ^{1}H NMR (500 MHz): δ 0.89 (t, 3H, *J* = 9.00 Hz, Me), 1.35 (m, 6H, 3 × CH_2), 1.98 (p, 2H, *J* = 7.5 Hz, NCH_2CH_2), 4.48 (t, 2H, *J* = 7.5 Hz, NCH_2), 7.25 (td, 1H, *J* = 7.00, 0.5 Hz, CH_{in}), 7.53 (td, 1H, *J* = 7.5, 1.5 Hz, CH_{in}), 7.77 (dd, 1H, *J* = 7.5, 1.5 Hz, CH_{in}), 7.87 (s, 1H, CH_{tr}), 8.17 (s, 1H, CHN), 8.48 (dd, 1H, *J* = 8.5, 1.0 Hz, CH_{in}). ^{13}C NMR (125.8 MHz): 14.0 (Me), 22.4, 26.1, 30.1, 31.2 (4 × CH_2), 51.1 (NCH_2), 112.8 (CH_{tr}), 113.0, 120.8, 122.2 (3 × CH_{in}), 124.8 (*ipso*-*C*), 128.0 (CH_{in}), 136.4 (NCH), 138.8 (*ipso*-*C*), 148.2 (*ipso*-*C*). HR-MS (FAB, +ve mode): calcd for $C_{15}H_{20}N_5$, 270.17132; found, 270.17134 $[M + H]^+$.

Preparation of 5a. A mixture of $[IrCl_2Cp^*]_2$ (60.0 mg, 0.076 mmol) and **3a** (43.0 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) was stirred for 4 h. The mixture was filtered through Celite and evaporated to dryness. The product was washed with hexane and precipitated from CH_2Cl_2/hexane to give **5a** as a yellow powder (31.0 mg, 73%). Anal. Calcd for $C_{25}H_{34}Cl_2N_5Ir$: C, 44.97; H, 5.13; N, 10.49. Found: C, 44.46; H, 5.05; N, 10.44%. ^{1}H NMR: δ 0.85 (t, 3H, *J* = 7 Hz, Me), 1.22 (m, 6H, 3 × CH_2), 1.66 (m, 17H, C_5Me_5 + NCH_2CH_2), 4.13 (t, 2H, *J* = 7.5 Hz, NCH_2), 7.36 (m, 2H, 2 × CH_{bi}), 7.97 (d, 1H, *J* = 8.0 Hz, CH_{bi}), 7.98 (s, 1H, CH_{tr}), 8.10 (d, 1H, *J* = 7.5 Hz, CH_{bi}), 9.35 (s, 1H, NCHN). ^{13}C NMR: δ 8.16 (C_5Me_5), 12.97 (Me), 21.38, 24.96, 29.21, 30.14 (4 × CH_2), 49.95 (NCH_2), 84.94 (C_5Me_5), 112.94 (CH_{tr}), 114.00, 119.26, 122.95, 124.55 (4 × CH_{bi}), 130.80, 138.99 (2 × C_{bi}), 139.92 (C_{tr}), 142.46 (NCHN).

Preparation of 5b. A mixture of $[IrCl_2Cp^*]_2$ (50.0 mg, 0.063 mmol) and **3b** (38.0 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was stirred for 4 h. The mixture was filtered through Celite and evaporated to dryness. The product was washed with hexane and precipitated from CH_2Cl_2/hexane to give **5b** as a yellow powder (60.0 mg, 63%). The product was recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{26}H_{28}Cl_2N_5Ir$: C, 46.36; H, 4.19; N, 10.40. Found: C, 46.48; H, 4.06; N, 10.42%. ^{1}H NMR: δ 1.66 (s, 15H, C_5Me_5), 5.31 (s, 2H, CH_2), 7.32 (m, 7H, Ph + 2CH_{bi}), 8.01 (s, 1H, CH_{tr}), 8.02 (d, 1H, *J* = 7.5 Hz, CH_{bi}), 8.14 (d, 1H, *J* = 7.5 Hz, CH_{bi}), 9.39 (s, 1H, NCHN). ^{13}C NMR: δ 9.16 (C_5Me_5), 54.15 (CH_2), 86.01 (C_5Me_5), 114.21 (CH_{tr}), 114.76, 120.21, 124.12, 125.59 (4 × CH_{bi}), 128.51, 128.55, 128.85 (3 × CH_{Ph}), 131.71 (C_{Ph}), 134.65, 139.96 (2 × C_{bi}), 141.26 (C_{tr}), 143.51 (NCHN). FAB-MS: 673 $[M]^+$, 638 $[M - Cl]^+$

Preparation of 7a. **3a** (150 mg, 0.55 mmol) was dissolved in MeCN (5 mL), and MeI (140 mg, 0.99 mmol) was added. The mixture was heated at 60 °C for 24 h in a sealed tube. The mixture was then filtered through Celite and evaporated to dryness. The product was washed with hexane and precipitated from CH_2Cl_2/hexane to give **7a** as a white powder (170 mg, 75%). The product was recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{16}H_{22}N_5I$: C, 46.72; H, 5.39; N, 17.03. Found: C, 46.63; H, 5.29; N, 16.99%. ^{1}H NMR: δ 0.91 (t, 3H, *J* = 7.0 Hz, H^{15}), 1.38 (m, 6H, 3 × CH_2), 2.03 (m, 2H, NCH_2CH_2), 4.28 (s, 3H, Me), 4.58 (t, 2H, *J* = 7.0 Hz, NCH_2), 7.79 (m, 2H, 2 × CH_{bi}), 8.07 (m, 1H, CH_{bi}), 8.13 (m, 1H, $CH_{tr}CH_{bi}$), 8.83 (s, 1H, CH_{tr}), 10.09 (s, 1H, NCHN). ^{13}C NMR: δ 12.32 (Me), 21.50, 25.13, 29.11, 30.27 (4 × CH_2), 32.75 (NMe), 50.64 (NCH_2), 112.82, 113.44 (2 × CH_{bi}), 118.03 (CH_{tr}), 126.92, 127.35 (2 × CH_{bi}), 129.79, 131.48, 138.23 (C_{tr}, 2 × C_{bi}), 140.78 (NCHN).

Preparation of 8a. A mixture of $[IrCl_2Cp^*]_2$ (60 mg, 0.076 mmol), **5a** (68 mg, 0.17 mmol), and NaOAc (15 mg, 0.19 mmol) in CH_2Cl_2 (5 mL) was stirred for 20 h. The mixture was filtered through

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Celite and evaporated to dryness. The product was washed with hexane and precipitated from CH_2Cl_2/hexane to give a yellow powder (50 mg, 40%). Anal. Calcd for $IrC_{26}H_{36}ClIN_5Ir$: C, 40.39; H, 4.69; N, 9.06. Found: C, 40.28; H, 4.60; N, 9.03%.^{1}H NMR: δ 0.87 (t, 3H, J = 7.0 Hz, Me), 1.33 (m, 6H, 3 × CH_2), 2.03 (s, 15H, C_5Me_5), 2.13 (m, 2H, NCH_2CH_2), 4.07 (s, 3H, NMe), 4.77 (t, 2H, J = 7.0 Hz, NCH_2), 7.44 (t, 1H, J = 8.0 Hz, H^3), 7.50 (d, 1H, J = 8.0 Hz, H^2), 7.59 (t, 1H, J = 8.0 Hz, H^4), 8.70 (d,1H, J = 8.0 Hz, H^5), 10.94 (s, 1H, H^9). ^{13}C NMR: δ 10.30 (C_5Me_5), 13.99 (Me), 22.51, 26.02, 29.97, 31.07 (4 × CH_2), 35.54 (NMe), 53.55 (NCH_2), 93.18 (C_5Me_5), 110.85 (C^2), 114.00 (C^5), 115.89(C^9), 125.10 (C^3), 126.76 (C^4), 129.27 (C^1), 135.35(C^6), 144.91 (C^8), 173.00 (C^7). FAB-MS: m/z 738 $[M]^+$, 611 $[M - I]^+$. ES-MS: m/z 738 $[M]^+$.

Preparation of 9a. A mixture of $[IrCl_2Cp^*]_2$ (29.0 mg, 0.037 mmol), the triazole **4a** (22.2 mg, 0.083 mmol), and KPF_6 (27 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was stirred for 20 h. The mixture was filtered through Celite and evaporated to dryness. The product was washed with hexane and precipitated from CH_2Cl_2/hexane to give **9a** as a yellow powder (38.0 mg, 65%). Anal. Calcd for $C_{25}H_{34}Cl_2N_5IrPF_6$: C, 38.63; H, 4.41; N, 9.01. Found: C, 38.72; H, 4.48; N, 8.93%. ^{1}H NMR: δ 0.89 (m, 3H, Me), 1.34 (m, 6H,3 × CH_2), 1.83 (s, 15H, C_5Me_5), 2.08 (m, 2H, NCH_2CH_2), 4.63 (t, 2H, J = 7.5 Hz, NCH_2), 7.37 (dd, 1H, J = 7.5, 8.0 Hz, H^4), 7.66 (dd, 1H, J = 7.5, 8.0 Hz, H^5), 7.86 (d, 1H, J = 8.0 Hz, H^6), 7.88 (d, 1H, J = 8.0 Hz, H^3), 8.46 (s, 1H, H^1), 8.59 (s, 1H, H^9). ^{13}C NMR: δ 9.02 (C_5Me_5), 13.94 (Me), 22.42, 26.00, 29.66, 30.99 (4 × CH_2), 53.72 (NCH_2), 89.51 (C_5Me_5), 110.63 (C^6), 111.19 (C^9), 122.34 (C^3), 124.81 (C^4), 124.91, 136.62, 142.64 (C^2,C^7,C^8), 132.30 (C^5), 138.68 (C^1). ES-MS: m/z 632 $[M]^+$. FAB MS: m/z 632 $[M]^+$

X-ray Crystal Structure Determinations. Data for **5b** were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo Kα radiation; λ = 0.7107 Å. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. The structures were solved by direct methods and with structure refinement on F^2 employed SHELXTL version 6.10.[23] Hydrogen atoms were included in calculated positions (C−H = 0.93−1.00 Å, O−H = 0.84 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5U_{eq} (O) for hydroxyl H atoms, 1.5U_{eq} (C) for methyl hydrogen atoms, and 1.2U_{eq} (C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters without positional restraints. Figures were drawn using the program ORTEP.[24] Crystal data for **5b**: $C_{26}H_{28}Cl_2IrN_5$; M = 673.63; triclinic; a = 8.0303(15) Å, b = 11.343(2) Å, c = 14.297(3) Å, α = 108.073(3)°, β = 98.709(3)°, γ = 90.588(3)°; V = 1221.5(4) Å^3; T = 150(2) K; space group $P\bar{1}$; Z = 2; 9508 reflections measured, 4729 independent reflections (R_{int} = 0.0423). The final R_1 values were 0.0413 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0879 ($I > 2\sigma(I)$). The final R_1 values were 0.0511 (all data). The final $wR(F^2)$ values were 0.0907 (all data).

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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