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Orthometalated Amino-Carbene Derivatives of Iridium via Anilines and Terminal Alkynes

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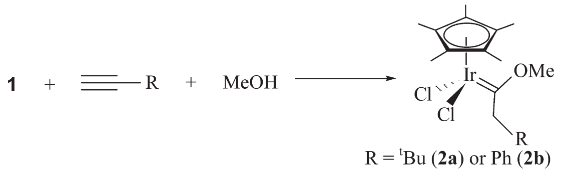
The reaction of a terminal alkyne (RCCH) and an aniline ($R'C_6H_4NH_2$) with the dinuclear species $[Cp^*IrCl_2]_2$ afforded cyclometalated amino-carbene derivatives $Cp^*Ir(Cl)[{=}C(CH_2R)NHC_6H_3R']$ via a hydroamination and an orthometalation. The reaction pathway has been examined through deuterium labeling and computational studies.

Introduction

The chemistry of transition metal carbene complexes has continued unabated from the synthesis of the first carbene complex,[1] through heteroatom-stabilized carbene complexes,[2] to their application as reactive intermediates in organic synthesis.[3] Fischer-type amino-carbene complexes are well recognized and have been proven to be useful in C−C bond formation reactions.[4] In the extensive literature on this class of carbene complexes, those of iridium are relatively rare and less extensively explored.[5] Most reports on their syntheses involve C−H bond activation of *N*-alkylamines, and although nucleophilic addition of amines onto coordinated alkynes is well established for a number of metal systems including those of ruthenium,[6] platinum,[7] and tungsten,[8] to our knowledge, there is no report on the synthesis of iridium amino-carbene complexes using this methodology.

Scheme 1



Earlier studies have shown that some iridium complexes can add alcohols onto coordinated terminal alkynes or alkylidenes in an intramolecular[9] or intermolecular[10] fashion. For example, we have reported that the dinuclear species $[Cp^*IrCl_2]_2$, **1**, reacts with terminal alkynes in the presence of methanol to afford iridium methoxy-carbene complexes **2** (Scheme 1). The reaction is believed to proceed via nucleophilic attack at the α-carbon of a vinylidene intermediate.

In this paper we wish to describe the analogous reaction involving anilines, which turned out to afford a general route to orthometalated iridium amino-carbene complexes.

Results and Discussion

Following the reaction scheme above, we expected that the reaction of **1** with a terminal alkyne (RCCH), and an aniline

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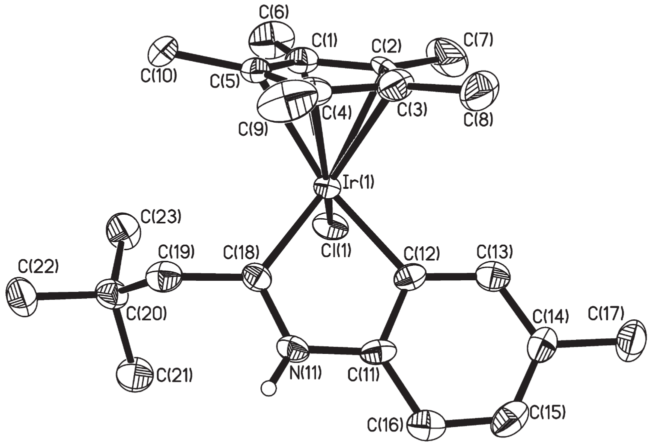
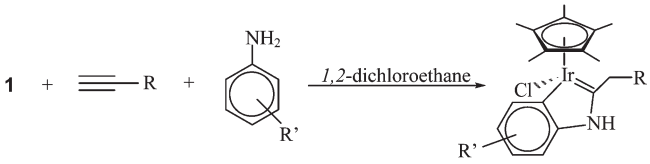


Figure 1. ORTEP plot (50% probability thermal ellipsoids) of **3b**. All but one H atom are omitted.

Scheme 2

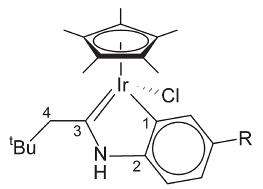


R = ^{t}Bu (**3**); R' = H (**a**), *4*-Me (**b**), *4*-Cl (**c**), *4*-OMe (**d**), *4*-NO$_2$ (**e**)
R = Ph (**4**); R' = H (**a**), *4*-Me (**b**), *4*-Cl (**c**), *4*-OMe (**d**), *4*-NO$_2$ (**e**)

($R'C_6H_4NH_2$) in place of methanol, would afford an iridium amino-carbene complex of the type [Cp*Ir(=C(NHC$_6$H$_4$R')(CH$_2$R))Cl$_2$]. Instead, we obtained orthometalated iridium amino-carbene complexes in yields from 30% to 80% for a wide variety of anilines and terminal alkynes; a selected sample for PhCCH and ^{t}BuCCH is shown in Scheme 2.

The reactions required typically a 20 equivalent excess of the alkyne; use of two equivalents gave incomplete reaction and the aniline addition product [Cp*IrCl$_2$NH$_2$C$_6$H$_4$R'], **5**;[11] changing solvents (to DCM, THF, or toluene) or temperature (to reflux) did not give any improvement. Attempts at extending the procedure to non-orthometalated carbene complexes, for example, with 2,6-disubstituted anilines such as 2,6-dichloroaniline and 2,6-difluoroaniline and with aliphatic amines such as benzylamine and 1-aminopentane, in the presence of 3,3-dimethyl-1-butyne were unsuccessful, giving only the corresponding analogues of **5**. In the case of 2,4,6-trimethylaniline, trace amounts of the C≡C triple bond cleavage product, viz., [Cp*Ir(Cl)(CO)(CH$_2$^{t}Bu)], **6**, were also formed. Aminolysis of the methoxy-carbene complexes **2**, a well-known synthetic route to amino-carbenes,[12] was also unsuccessful and gave **6** instead. The failure of this route may be attributed to the deprotonation of adventitious water, thus favoring hydroxide attack on **2**; these are known to decompose in the presence of aqueous KOH to afford **6**. The reaction is otherwise fairly robust, as it appears unaffected by the presence of water; in the absence of aniline, C≡C triple bond cleavage to **6** occurs.[10] There were also no indications of alkyne polymerization or hydroamination under these conditions.

Table 1. Common Atomic Numbering Scheme and Selected Bond Parameters for 3a and 3b



	3a	**3b**
	Bond Lengths (Å)	
Ir−Cl	2.385(2)	2.4085(14)
Ir−C(1)	2.047(9)	2.037(5)
Ir−C(3)	1.992(9)	1.991(6)
N−C(2)	1.428(12)	1.398(8)
N−C(3)	1.291(11)	1.314(8)
C(1)−C(2)	1.381(12)	1.386(8)
C(3)−C(4)	1.496(12)	1.501(9)
	Bond Angles (deg)	
C(1)−Ir−C(3)	78.1(4)	78.4(2)
C(2)−N−C(3)	117.2(7)	117.0(5)
C(1)−C(2)−N	112.3(8)	113.4(5)
N−C(3)−Ir	117.7(7)	116.8(4)

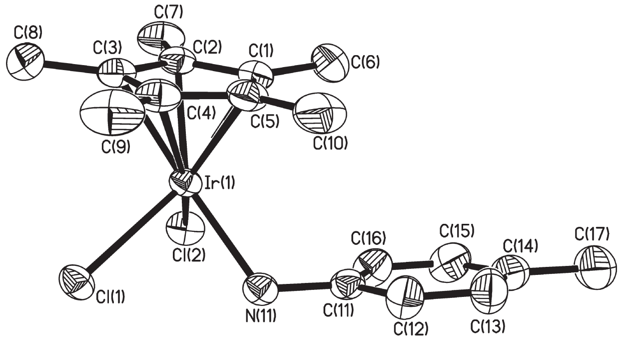


Figure 2. ORTEP plot (50% probability thermal ellipsoids) of **5b**. H atoms are omitted. Selected bond lengths (Å) and angles (deg): Ir(1)−N(11) = 2.169(3); Ir(1)−Cl(2) = 2.4033(7); Ir(1)−Cl(1) = 2.4315(7); N(11)−C(11) = 1.453(4); N(11)−Ir(1)−Cl(2) = 83.31(8); N(11)−Ir(1)−Cl(1) = 80.67(7); Cl(2)−Ir(1)−Cl(1) = 87.50(3).

The products **3**−**5** have all been characterized spectroscopically and analytically, and the structures of **3a**, **3b**, and **5b** have also been confirmed by single-crystal X-ray diffraction studies. The ORTEP plot for **3b** is shown in Figure 1, while a common atomic numbering scheme and selected bond parameters for **3a** and **3b** are given in Table 1; the ORTEP plot and selected bond parameters for **5b** are shown in Figure 2. Similar carbene complexes that contain an iridacycle that have been structurally characterized include Tp^{Ph}-Ir(H)(=CHNMepy),[13] {Ir(H)$_2$(=CMeNEtpy)(PPh$_3$)$_2$}$^{+}$,[14] and {Ir(H)$_2$(=C[CH$_2$CH$_2$CH$_2$Ph]NMepy)(PPh$_3$)$_2$}$^{+}$.[15] The ^{1}H NMR

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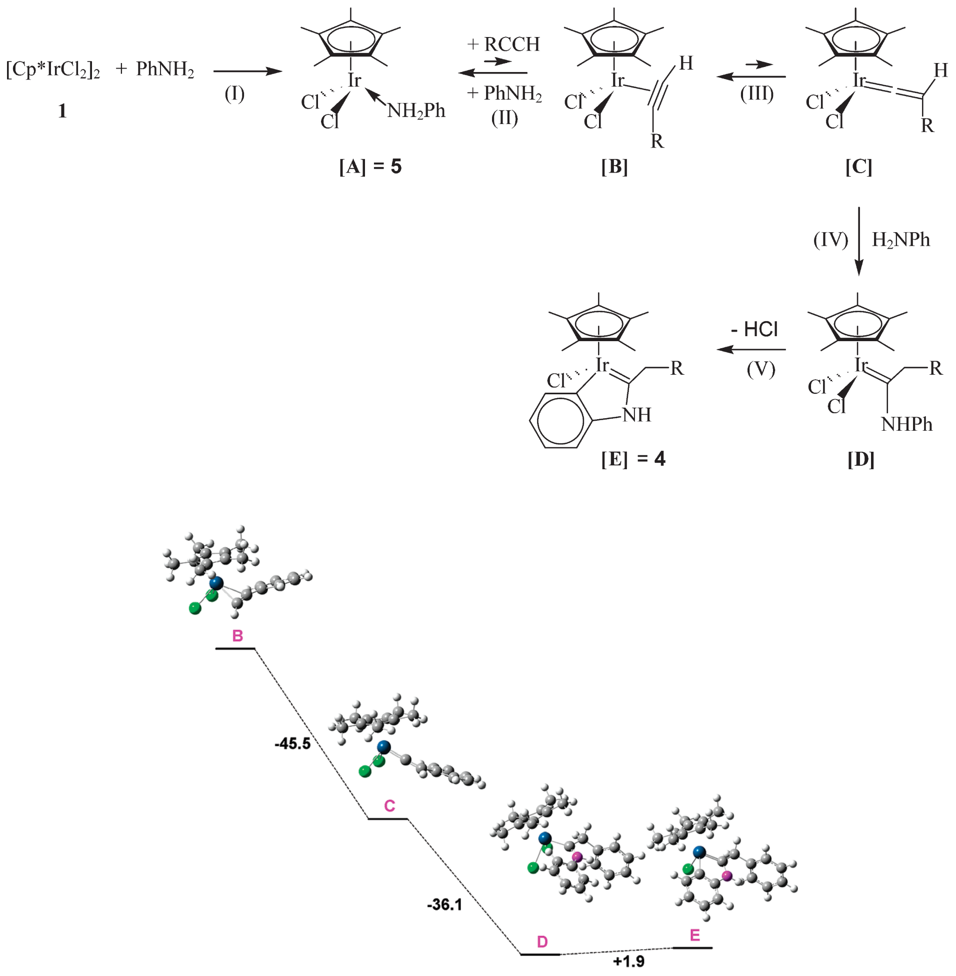
Scheme 3[a]



[a] Ir = blue; Cl = green; N = pink; C = large, gray; H = small, gray.

[a] Ir = blue; Cl = green; N = pink; C = large, gray; H = small, gray.

spectra of the amino-carbene complexes were characterized by the two doublet resonances arising from the two diastereotopic protons and the broad NH singlet resonance at ~10 ppm. The carbene carbon exhibited a resonance at 220−233 ppm in the $^{13}C\{^1H\}$ NMR spectra, as is typical for a transition metal carbene. The carbene nature of C(3) is indicated by the significantly longer Ir−C(1) bond length compared to the Ir−C(3) bond length, a difference of ~8σ in both **3a** and **3b**. Interestingly, both these bonds are longer than the corresponding bonds (2.015(3) and 1.930(3) Å, respectively) in the most similar iridacycle, Tp^{Ph}Ir(H)(=CHNMepy). These are presumably a result of the different bonding nature (soft vs hard) of Cp* vs Tp^{Ph}.[16] There also appears to be significant double-bond character in the C−N bonds, however, as the N−C(3) and N−C(2) bond lengths (1.314(8) and 1.398(8) Å, and 1.291(11) and 1.428(12) Å, in **3a** and **3b**, respectively) are significantly shorter than the N(11)−C(11) bond (1.453(4) Å) in **5b**. This is also consistent with the ~117° C(2)−N−C(3) bond angle, which is indicative of sp^2 hybridization at the N atom.

Mechanistic Considerations. That the reactions afforded **5** in the absence of a large excess of the alkynes suggested that it may be involved in the reaction pathway. This was shown to be the case when it was found that the reaction of aniline with **1** formed **5a** almost immediately and in good yields, and subsequent reaction of it with excess alkynes afforded **3** or **4** in similar yields to the one-pot reaction. This latter reaction proceeded more slowly; monitoring the reaction of ^{t}BuCCH with **5a** showed complete consumption of **5a** after about 12 h. Addition of ^{t}BuCCH and an equivalent of 4-methoxyaniline to a sample of **5a** afforded **3a** and **3d** in a 1:3 ratio, pointing to the easy dissociation of the aniline ligand from **5a** and suggesting that it acts as an intermediary for the cleavage of **1**. A proposed reaction pathway is shown in Scheme 3. The energetics for this has also been examined computationally with DFT at the B3LYP/LANL2DZ level, as for the earlier study, and the computed energies (ΔG^o) from **B** onward (in kJ mol^{-1}) are given.[10]

Although no kinetic barriers were computed, the negative or small computed energies involved in the steps suggest that the reaction pathway is reasonable. With the exception of the formation of **A** (or **5**) and the final orthometalation step, the pathway is similar to that proposed earlier for the C≡C triple bond cleavage reaction. Presumably, in the presence of an excess of the appropriate alkyne, the coordinated aniline is replaced, and the alkyne species **B** rapidly rearranges to the vinylidene complex **C**. Step III was believed to involve deprotonation−protonation for the 1,2-shift, and in accord with that,[10] the reaction of **1** with PhCCD and aniline showed no deuterium incorporation in the product **4a**. Step

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Table 2. Amount of Reagent Used, Product Formed, and Elemental Analyses and HRMS Data for Products[a]

aniline	alkyne	product (mg, %)	elemental analysis	HRMS
$C_6H_5NH_2$ (9 μL, 100 μmol)	^{t}BuCCH	$C_{22}H_{31}ClIrN$, **3a** (43.7, 81)	Found: C, 48.95; H, 6.08; N, 2.98 Calc: C, 49.19; H, 5.82; N, 2.61	Found: 502.2074 Calc $[M - Cl]^+$: 502.2087
4-$MeC_6H_4NH_2$ (10.7 mg, 100 μmol)	^{t}BuCCH	$C_{23}H_{33}ClIrN$, **3b** (43.7, 79)	Found: C, 50.23; H, 6.35; N, 2.75 Calc: C, 50.12; H, 6.03; N, 2.54	Found: 516.2247 Calc $[M - Cl]^+$: 516.2243
4-$ClC_6H_4NH_2$ (12.8 mg, 100 μmol)	^{t}BuCCH	$C_{22}H_{30}Cl_2IrN$, **3c** (57.3, 72)	Found: C, 45.97; H, 5.03; N, 2.12 Calc: C, 46.23; H, 5.29; N, 2.45	Found: 536.1682 Calc $[M - Cl]^+$: 536.1688
4-$MeOC_6H_4NH_2$ (12.4 mg, 100 μmol)	^{t}BuCCH	$C_{23}H_{33}ClIrNO$, **3d** (56.9, 81)	Found: C, 48.96; H, 6.05; N, 2.61 Calc: C, 48.70; H, 5.86; N, 2.47	Found: 532.2186 Calc $[M - Cl]^+$: 532.2192
4-$O_2NC_6H_4NH_2$ (13.8 mg, 100 μmol)	^{t}BuCCH	$C_{22}H_{30}ClIrN_2O_2$, **3e** (44.4, 76)	Found: C, 45.09; H, 5.04; N, 4.61 Calc: C, 45.39; H, 5.19; N, 4.81	Found: 547.1923 Calc $[M - Cl]^+$: 547.1937
$C_6H_5NH_2$ (9 μL, 100 μmol)	PhCCH	$C_{24}H_{27}ClIrN$, **4a** (35.8, 64)	Found: C, 52.05; H, 4.91; N, 2.64 Calc: C, 51.74; H, 4.88; N, 2.51	Found: 522.1765 Calc $[M - Cl]^+$: 522.1774
4-$MeC_6H_4NH_2$ (10.7 mg, 100 μmol)	PhCCH	$C_{25}H_{29}ClIrN$, **4b** (40.7, 71)	Found: C, 52.16; H, 5.41; N, 2.53 Calc: C, 52.57; H, 5.12; N, 2.45	Found: 536.1927 Calc $[M - Cl]^+$: 536.1931
4-$ClC_6H_4NH_2$ (12.8 mg, 100 μmol)	PhCCH	$C_{24}H_{26}Cl_2IrN$, **4c** (40.9, 69)	Found: C, 48.91; H, 4.56; N, 2.35 Calc: C, 48.73; H, 4.43; N, 2.37	Found: 556.1362 Calc $[M - Cl]^+$: 556.1376
4-$MeOC_6H_4NH_2$ (12.4 mg, 100 μmol)	PhCCH	$C_{25}H_{29}ClIrNO$, **4d** (43.0, 73)	Found: C, 51.16; H, 4.98; N, 2.51 Calc: C, 51.14; H, 5.05; N, 2.39	Found: 552.1872 Calc $[M - Cl]^+$: 552.1879
4-$O_2NC_6H_4NH_2$ (13.8 mg, 100 μmol)	PhCCH	$C_{24}H_{26}ClIrN_2O_2$, **4e** (39.3, 65)	Found: C, 48.05; H, 4.25; N, 4.76 Calc: C, 47.87; H, 4.35; N, 4.65	Found: 567.1620 Calc $[M - Cl]^+$: 567.1625

[a] In all experiments, amounts of reagents used are: **1** (40 mg, 50 μmol), ^{t}BuCCH (125 μL, 100 μmol), or PhCCH (110 μL, 100 μmol).

Table 3. ^{1}H and ^{13}C{^{1}H} NMR Data for 3 and 4

compound	^{1}H NMR data	^{13}C{^{1}H} NMR data
3a	1.16 (s, 9H, ^{t}Bu), 1.77 (s, 15H, Cp*), 2.77 (d, $^2J_{HH}$ = 12.6, 1H, CH_2), 3.64 (d, 1H, CH_2), 6.91 (m, 1H, aromatic), 6.99 (m, 1H, aromatic), 7.18 (m, 1H, aromatic), 7.56 (m, 1H, aromatic), 9.93 (s, 1H, NH)	9.68 (CH_3, Cp*), 30.99 (CH_3, ^{t}Bu), 35.36 (C, ^{t}Bu), 60.00 (CH_2), 95.04 (C, Cp*), 112.38, 122.58, 125.35 and 135.53, (aromatic CH), 144.89 and 151.00 (aromatic C), 227.44 (Ir=C)
3b	1.15 (s, 9H, ^{t}Bu), 1.77 (s, 15H, Cp*), 2.34 (s, Me), 2.75 (d, $^2J_{HH}$ = 12.6 Hz, 1H, CH_2), 3.61 (d, 1H, CH_2), 6.72 (m, 1H, aromatic), 7.07 (m, 1H, aromatic), 7.36 (m, 1H, aromatic), 9.90 (s, 1H, NH)	9.68(CH_3, Cp*), 21.68 (CH_3, Ar), 30.98 (CH_3, ^{t}Bu), 35.30 (C, ^{t}Bu), 59.81(CH_2), 94.78 (C, Cp*), 112.09, 123.16, and 136.16 (CH, aromatic), 134.57, 144.92, and 148.76 (C, aromatic), 225.77 (Ir=C)
3c	1.15 (s, 9H, ^{t}Bu), 1.77 (s, 15H, Cp*), 2.77 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2), 3.63 (d, 1H, CH_2), 6.90 (m, 1H, aromatic), 7.11 (m, 1H, aromatic), 7.47 (m, 1H, aromatic), 9.91 (s, 1H, NH)	9.66 (CH_3, Cp*), 31.00 (CH_3, ^{t}Bu), 35.44 (C, ^{t}Bu), 60.05 (CH_2), 95.30 (C, Cp*), 113.20, 122.43, and 134.81 (CH, aromatic), 129.77, 146.97, and 149.70 (C, aromatic), 227.73 (Ir=C)
3d	1.15 (s, 9H, ^{t}Bu), 1.77 (s, 15H, Cp*), 2.75 (d, $^2J_{HH}$ = 12.6 Hz, 1H, CH_2), 3.58 (d, 1H, CH_2), 3.82 (s, OMe), 6.48 (m, 1H, aromatic), 7.11 (m, 1H, aromatic), 7.14 (m, 1H, aromatic), 9.89 (s, 1H, NH)	9.65 (CH_3, Cp*), 30.97 (CH_3, ^{t}Bu), 35.19 (C, ^{t}Bu), 55.56 (OMe), 59.70 (CH_2), 94.66 (C, Cp*), 107.29, 112.91, and 120.90 (CH, aromatic), 145.10, 146.92, and 156.88 (C, aromatic), 223.91 (Ir=C)
3e	1.17 (s, 9H, ^{t}Bu), 1.80 (s, 15H, Cp*), 2.80 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2), 3.70 (d, 1H, CH_2), 7.26 (m, 1H, aromatic), 7.85 (m, 1H, aromatic), 8.41 (m, 1H, aromatic), 10.04 (s, 1H, NH)	9.73 (CH_3, Cp*), 31.06 (CH_3, ^{t}Bu), 35.96 (C, ^{t}Bu), 60.56 (CH_2), 96.48 (C, Cp*), 111.53, 120.02, and 130.26 (CH, aromatic), 144.32, 145.49, and 156.62 (C, aromatic), 233.64 (Ir=C)
4a	1.87 (s, 15H, Cp*), 4.58 (d, $^2J_{HH}$ = 18.8 Hz, 1H, CH_2), 4.76 (d, 1H, CH_2), 6.84−6.87 (m, 1H, aromatic), 6.95−6.99 (m, 2H, aromatic), 7.27 (m, 2H, aromatic), 7.39−7.46 (m, 3H, aromatic), 7.68 (m, 1H, aromatic), 9.50 (s, 1H, NH)	9.65 (CH_3, Cp*), 52.80 (CH_2), 94.07 (C, Cp*), 113.40, 122.41, 125.60, 128.12, 129.75, 130.39, and 135.28 (CH, aromatic), 134.48, 144.50, and 151.10 (C, aromatic), 224.22 (Ir=C)
4b	1.87 (s, 15H, Cp*), 2.34 (s, Me), 4.55 (d, $^2J_{HH}$ = 19.0 Hz, 1H, CH_2), 4.73 (d, 1H, CH_2), 6.65 (m, 1H, aromatic), 6.87 (m, 1H, aromatic), 7.25−7.27 (m, 2H, aromatic), 7.38−7.48 (m, 4H, aromatic), 9.47 (s, 1H, NH)	9.65 (CH_3, Cp*), 21.66 (CH_3, Ar), 52.75 (CH_2), 93.83 (C, Cp*), 113.04, 123.01, 128.13, 129.71, 130.38, 134.72, 134.86, 135.93, 144.58, and 148.92 (aromatic), 222.76 (Ir=C)
4c	1.86 (s, 15H, Cp*), 4.55 (d, $^2J_{HH}$ = 19.2 Hz, 1H, CH_2), 4.72 (d, 1H, CH_2), 6.82 (m, 1H, aromatic), 6.91 (m, 1H, aromatic), 7.25 (m, 2H, aromatic), 7.39−7.46 (m, 3H, aromatic), 7.58 (m, 1H aromatic), 9.53 (s, 1H, NH)	9.61 (CH_3, Cp*), 52.88 (CH_2), 94.30 (C, Cp*), 114.26, 122.19, 128.29, 129.79, 130.20, 130.35, 134.32, 134.56, 146.79, and 149.76 (aromatic), 225.14 (Ir=C)
4d	1.87 (s, 15H, Cp*), 3.82 (s, OMe), 4.54 (d, $^2J_{HH}$ = 19.0 Hz, 1H, CH_2), 4.70 (d, 1H, CH_2), 6.41 (m, 1H, aromatic), 6.91 (m, 1H, aromatic), 7.24−7.27 (m, 3H, aromatic), 7.38−7.45 (m, 3H, aromatic), 9.46 (s, 1H, NH)	9.61 (CH_3, Cp*), 52.53 (CH_2), 55.48 (OMe), 93.75 (C, Cp*), 107.09, 113.91, 120.63, 128.12, 129.69, and 130.39 (CH, aromatic), 134.67, 145.21, 146.57, and 157.00 (C, aromatic), 220.88 (Ir=C)
4e	1.89 (s, 15H, Cp*), 4.58 (d, $^2J_{HH}$ = 19.0 Hz, 1H, CH_2), 4.78 (d, 1H, CH_2), 7.08 (m, 1H, aromatic), 7.25−7.27 (m, 2H, aromatic), 7.40−7.48 (m, 3H, aromatic), 7.76 (m, 1H, aromatic), 8.51 (m, 1H, aromatic), 9.78 (s, 1H, NH)	9.65 (CH_3, Cp*), 53.58 (CH_2), 95.35 (C, Cp*), 113.01, 113.51, 119.48, 126.51, 128.52, 129.92, 130.31, 133.94, 144.47, 145.53, and 156.73 (aromatic), 231.29 (Ir=C)

IV, from **C** to the proposed amino-carbene complex intermediate **D**, is a hydroamination step and also has an analogue in the C≡C triple bond cleavage reaction. The ΔG^o associated with this step in both reactions (an alkyne hydroamination vs a hydration) are also comparable: −36 and −69 kJ mol^{-1}, respectively. There are at least two alternative mechanisms for this step: A nucleophilic attack by aniline at the vinylidene α-carbon atom (to a zwitterions) followed by proton transfer (may be intramolecular or intermolecular)[6g] or via a concerted process involving a four-membered transition state.[6b] That the reaction solvent is rather nonpolar tends to disfavor the first alternative, although it cannot be ruled out at this point.

Isotopic labeling experiments employing (a) aniline and ^{t}BuCCH in the presence of D_2O, (b) d_7-aniline and ^{t}BuCCH, and (c) d_5-aniline and ^{t}BuCCH afforded **3a** with both, one, or none, respectively, of the diastereotopic CH_2 protons being deuterated. These results are consistent with the source for each of these protons being water and aniline; an intermolecular proton transfer for step IV is therefore unlikely, as that would be expected to involve water or free aniline.

The final step is an orthometalation,[6a] and the $\Delta G^{\underline{\circ}}$ has been computed to be +1.9 kJ mol^{-1}; this would most certainly become considerably negative in the presence of moisture (ΔG_{298} for formation of hydrochloric acid is about −96 kJ mol^{-1})[17] and is probably the driving force for the reaction.

Concluding Remarks

In this study, we have reported a facile synthetic route to amino-carbene derivatives of iridium(III) from the reaction of anilines and terminal alkynes with the readily available dinuclear species $[Cp^*IrCl_2]_2$. Deuteration and computational studies suggest that the reaction pathway is very similar to that followed in the C≡C triple bond cleavage reaction with water and involves a hydroamination step. Further work to examine the extension of this synthetic methodology to other heteroatom-substituted carbenes, as well as cleavage of the carbene fragment, is underway.

Experimental Section

General Procedures. All reactions and manipulations, except for TLC separations, were performed under argon by using standard Schlenk techniques. The starting material **1** was prepared according to the published method.[18] All other chemicals were from commercial sources and used as supplied without further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ on a JEOL ECA400 or ECA400SL spectrometer and were referenced to residual solvent resonances. High-resolution mass spectra (HRMS) were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by the microanalytical laboratory in NTU.

Reaction of 1 with Alkyne and Aniline. In a typical reaction, to a solution of **1** (40 mg, 50 μmol) and 3,3-dimethyl-1-butyne (125 μL, 20-fold excess) in 1,2-dichloroethane (4 mL) was added aniline (9 μL, 100 μmol). There was an immediate color change from bright orange to yellow, and upon overnight stirring, it turned orange. The solvent was then removed under reduced pressure, and the residue obtained was dissolved in the minimum amount of dichloromethane for chromatographic separation on silica gel TLC plates. Elution with hexane/ethylacetate (3:2, v/v) yielded **3a** as a yellow solid.

Similar procedures were used with the other alkynes and anilines, and these are summarized in Tables 2 and 3.

Crystallographic Studies. Diffraction quality crystals were grown by slow cooling from dichloromethane and then mounted onto quartz fibres. X-ray data were collected at 223 K on a Bruker X8 APEX system, using Mo Kα radiation, with the SMART suite of programs.[19] Data were processed and corrected for Lorentz and polarization effects with SAINT,[20] and for absorption effects with SADABS.[21] Structural solution and refinement were carried out with the SHELXTL suite of programs.[22]

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The amine hydrogens were located via low-angle difference maps and refined, while the organic hydrogen atoms were placed in calculated positions and refined with a riding model. A disordered dichloromethane solvate was found in **3b**, which was modeled over two symmetry-related sites with a total occupancy of 0.25 and appropriate restraints placed. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

Computational Studies. The reaction energetics were studied using DFT theory utilizing Becke's three-parameter hybrid function[23] and Lee−Yang−Parr's gradient-corrected correlation function[24] (B3LYP), together with the LanL2DZ (Los Alamos effective core potential double-ζ) basis set. Spin-restricted calculations were used for geometry optimization, and harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies and to evaluate zero-point energy (ZPE) corrections. All calculations were performed using the Gaussian 03 suite of programs.[25]

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Supporting Information Available: Crystallographic data in CIF format, experimental details and characterization for other amino-carbene complexes, and details of deuterium labeling experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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