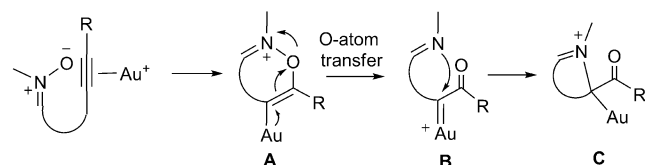


Isolation of Azomethine Ylides and Their Complexes: Iridium(III)-Mediated Cyclization of Nitrone Substrates Containing Alkynes**

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Efficient, atom-economic, and selective construction of useful heterocycles from readily available starting materials remain an important task in synthetic chemistry.^[1] Cyclization of functionalized alkynes and alkenes represents an important strategy in this regard. It is well known that Lewis-acidic metals, particularly gold(I) and platinum(II), can activate alkynes towards the attack of carbon, oxygen, and nitrogen nucleophiles, thus leading to the construction of new skeletons.^[2] This research area is rapidly growing owing to the unique properties of these metals in promoting two or more mechanistically distinct reactions in a tandem process to achieve molecular complexity from simple starting materials.^[2]

Among the various nucleophiles that are known to attack alkynes, nitrone,^[3,4] nitro,^[5] sulfoxide,^[6] and amine *N*-oxide^[7] groups are particularly interesting. Nucleophilic attack of these polar N⁺–O[–] groups on alkynes gives metal vinyl species^[8] bearing a positively charged electrophilic center (**A**, Scheme 1; shown for endo cyclization only). These vinyl

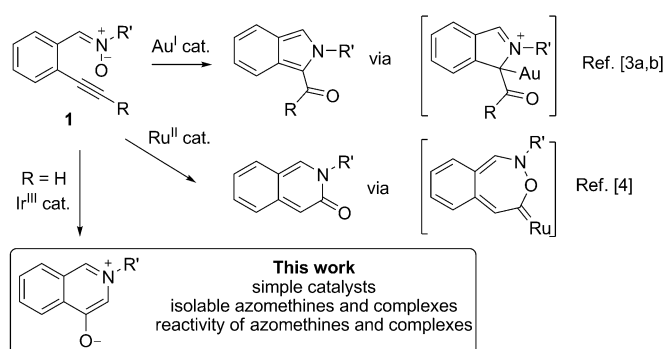


Scheme 1. Azomethine intermediates obtained through redox cyclization.

intermediates^[8c] can undergo subsequent ring opening and N–O bond cleavage to afford reactive metal α -oxo carbenoids **B** through an addition-elimination process that results in an internal oxygen-atom transfer. Such metal α -oxo carbenoids

have been proposed in an increasing number of reports and are susceptible to the attack of a series of nucleophiles including amines, arenes, and migrating hydrides and alkyls, thus enabling skeleton manipulation.^[3–5] This chemistry has been recently reviewed by us.^[9] In the case of a nitrone substrate containing an alkyne, an α -oxo carbenoid intermediate bearing a proximal imine group is generated, and intramolecular nucleophilic addition can lead to the metal azomethine intermediate **C** (Scheme 1) that can be additionally functionalized for structure diversification.^[3] However, neither the free azomethine ylide nor its complex has been isolated.

Two distinct types of products have been reported in the redox cyclization of nitrone alkynes (Scheme 2). Gold(I)-catalyzed cyclization of nitrone alkynes **1** afforded isoindoles



Scheme 2. Cyclization of nitrone alkynes.

with the intermediacy of both an oxo carbenoid (type **B**) and a five-membered azomethine gold species (type **C**).^[3a] In contrast, TpRu^{II}-catalyzed (Tp = tris(1-pyrazolyl)borate) cyclization of such terminal alkynes yielded 3-isoquinolones without forming intermediate α -oxo carbenoid species.^[4] Despite the successful handling of oxo carbenoids as key intermediates in catalysis, many questions remain unsolved. We initiated our studies on this type of chemistry with the following questions: 1) Can we use other readily available catalysts to shift selectivity of the cyclization of **1** to other heterocycles (particularly azomethine ylides)? 2) Can we isolate azomethine ylides and their metal complexes? 3) What are the structures and reactivity of azomethine ylides and their complexes? Ylidic ligands^[10] often offer unusual properties in organometallic chemistry. Studies on the intrinsic aspects of such reactive intermediates should provide important insight into the development of synthetic methodologies.

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The redox cyclization of alkynes bearing a polar N–O bond is not limited to mediation using gold and platinum. Crabtree and co-workers have reported stoichiometric intramolecular O-atom transfer from a nitro group to an alkyne mediated by iridium(III) hydrides.^[11] Our objective was to use electrophilic iridium(III) complexes for the redox cyclization of nitron alkynes for different selectivity. In fact, we have noted strong Lewis acidity of $[\text{IrCp}^*\text{Cl}_2]_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in the coordination reaction with *N*-alkylimidazoles,^[12] wherein two *N*-alkylimidazole molecules are readily coordinated to an iridium center to give an ionic complex. We reasoned that this electrophilicity may be extended to the activation of alkynes toward the attack of polar N–O bonds such as those found in nitrones. We report herein our studies on the synthesis, structure, and reactivity of azomethine ylides and their metal complexes.

Gratifyingly, slow heating of a mixture of nitron alkyne **1a** and $[\text{IrCp}^*\text{Cl}_2]_2$ (0.5 equiv) in MeCN afforded red microcrystals together with a red solution, from which product **2a** was isolated as an air-stable solid in 84% yield [Eq. (1)]. Compound **2a** was fully characterized, including X-ray crystallography (see Figure 1). ^1H and ^{13}C NMR spectroscopy revealed that one equivalent of the nitron alkyne was incorporated. In the ^1H NMR spectrum of **2a**, two singlet signals in the aromatic region were detected, and in the

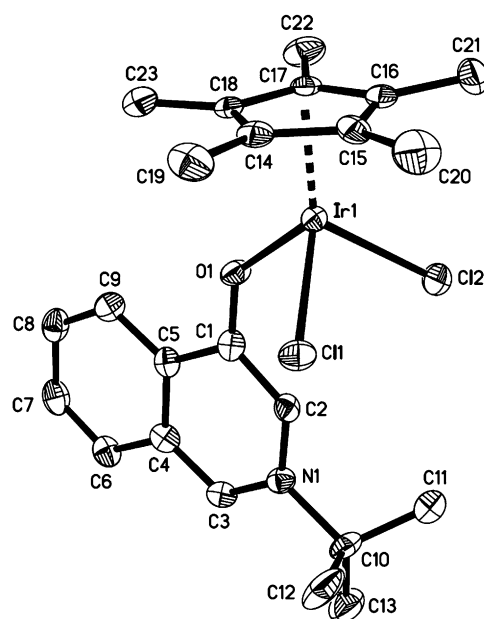
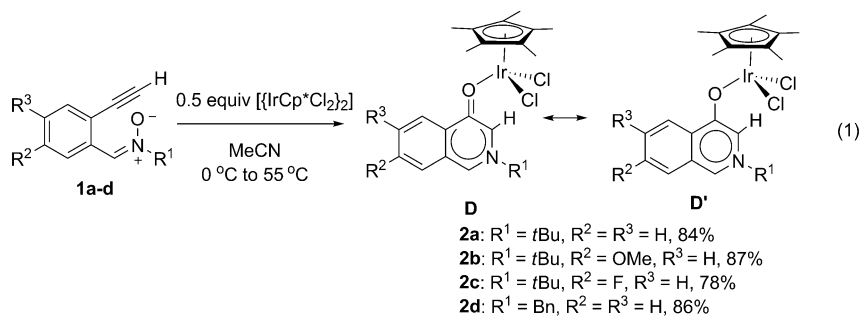


Figure 1. Molecular structure of **2a** is shown with 50% thermal ellipsoids.^[17] Selected lengths [Å]: Ir(1)–O(1) 2.150(3), Ir(1)–Cl(1) 2.429(1), Ir(1)–Cl(2) 2.414(1), O(1)–C(1) 1.293(4), C(1)–C(2) 1.390(6), C(4)–C(5) 1.437(5), C(6)–C(7) 1.351(6), C(8)–C(9) 1.366(5).



^{13}C NMR spectrum (CD_2Cl_2), a rather low-field resonance signal ($\delta = 166.5$ ppm) was observed and assigned to the O–C group. Thus this transformation represents a formal O-atom transfer from the nitron to the internal carbon atom of the alkyne unit.

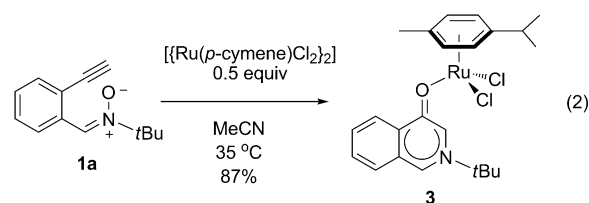
The identity of product **2a** was unambiguously confirmed by X-ray crystallography (Figure 1). The coordination sphere of complex **2a** includes a Cp^* ring, two chlorides, and the oxygen atom of an ylidic azomethine. We would expect the oxygen atom to bind as an anionic donor as in an aryl oxide ligand. However, a surprisingly short C(1)–O(1) distance (1.293(4) Å) was detected in this azomethine unit, thus indicating that this bond has a significant double bond character. Therefore, this ligand is best described as an unusual neutral O donor in a carbonyl moiety embedded within an azomethine ylide, wherein charges are delocalized throughout the fused aromatic system. In contrast to other C–C bonds in the azomethine ring, the C(8)–C(9) (1.366(5) Å) and C(6)–C(7) (1.351(6) Å) bonds are rather short and are essentially double bonds. Thus both **D** and **D'** [Eq. (1)] are

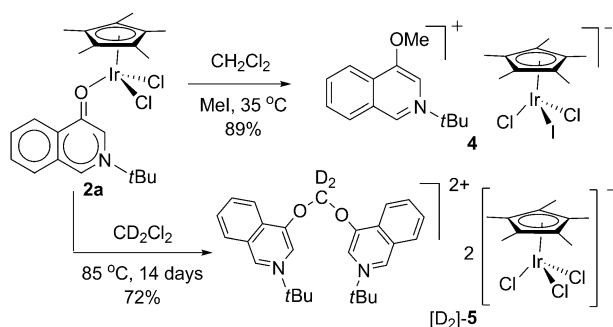
reasonable resonance structures, but **D** is expected to be the major contributor. We noted that synthesis of gold complexes of azomethines has been attempted, but with no success.^[3b]

Under these reaction conditions other iridium azomethine complexes were prepared in 78–87% yield by using *N*-*tert*-butyl and *N*-benzyl nitrones. However, no reaction occurred when a nitron substrates containing internal alkynes were employed even at a

higher temperature (80 °C). In addition, extension of the scope of this reaction to the rhodium congener $[\text{RhCp}^*\text{Cl}_2]_2$ met with failure and no reaction occurred, possibly because of its low electrophilicity. In contrast, isostructural complex **3** was successfully isolated in 87% yield when **1a** and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ were reacted in MeCN [Eq. (2)].

We felt that the azomethine ligand in complexes **2a–d** should be somewhat labile. Indeed, heating a CH_2Cl_2 solution of **2a** and MeI readily afforded the ionic complex **4** in 89% yield (Scheme 3); the ligand dissociation and a subsequent $\text{S}_{\text{N}}2$ reaction seems a plausible pathway. Moreover, much less

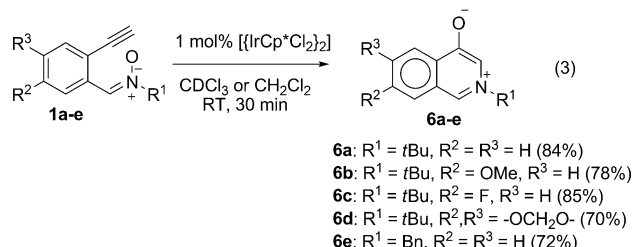




Scheme 3. Reactivity of iridium azomethine complexes.

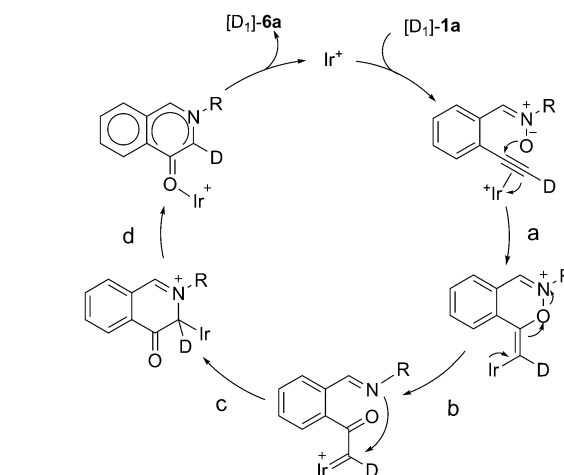
reactive electrophiles such as CD_2Cl_2 can slowly react with **2a** to furnish product $[\text{D}_2]\text{-5}$ (72 %), which was characterized by NMR spectroscopy and ESI-MS.

The lability of this azomethine ligand bodes well for catalytic synthesis of azomethines. Excitingly, $[\{\text{IrCp}^*\text{Cl}_2\}_2]$ proved to be a highly efficient catalyst for cyclizing **1a** into azomethine ylide **6a** in 96 % yield (NMR) and 84 % yield (isolated), and even a 1 mol % loading of the catalyst is sufficient at room temperature. In accordance with the poor reactivity of $[\{\text{RhCp}^*\text{Cl}_2\}_2]$ in stoichiometric reactions with **1a**, $[\{\text{RhCp}^*\text{Cl}_2\}_2]$ failed to catalyze the cyclization of **1a**. In comparison, $[\{\text{Ru}(p\text{-cymene})\text{Cl}_2\}_2]$ (2 mol %) is an active catalyst, and the azomethine product was generated in comparably high yield (92 %), albeit after a longer reaction time. Under the iridium catalysis, nitron alkyne **1a–e** bearing various substituents on both the aryl ring and the N, cyclized smoothly. Thus free azomethine ylides **6a–e** were successfully isolated (70–84 %) as low-melting solids after column chromatography [Eq. (3)]. In the IR spectrum of **6a**, the signal for the C–O group appears at 1570 cm^{-1} , and in the



^{13}C NMR spectrum (CD_2Cl_2) a low-field signal ($\delta = 168.0\text{ ppm}$) was detected for the carbonyl carbon atom. These indications all point to a certain amount of double bond character.^[13]

Complex **2a** is the only iridium species observed in the catalytic cyclization of **1a**. In addition, when complex **2a** (1 mol %) was employed as a catalyst for the cyclization of **1a**, azomethine **6a** was obtained at a rate comparable to that when using $[\{\text{IrCp}^*\text{Cl}_2\}_2]$ as a catalyst, thus supporting the intermediacy of an O-bound azomethine complex in the catalytic cycle. Deuterium labeling experiments were carried out to probe the mechanism. Cyclization of $[\text{D}_1]\text{-1a}$ (deuterated at the alkynyl position) using $[\{\text{IrCp}^*\text{Cl}_2\}_2]$ (1 mol %) afforded product $[\text{D}_1]\text{-6a}$ in 95 % yield (NMR), and no deuterium scrambling was detected, thereby suggesting that no cleavage of the alkynyl C–H bond is involved. To further confirm this conclusion, a crossover experiment was carried out using an equimolar mixture of $[\text{D}_1]\text{-1a}$ and **1e**. Both $[\text{D}_1]\text{-6a}$ and **6e** were obtained (see the Supporting Information), and the crossover product was not detected by ^1H NMR spectroscopy, thus indicating that no alkyne–vinylidene rearrangement is involved. This is in contrast to the proposed vinylidene intermediates in $[\{\text{Cp}^*\text{IrCl}_2\}_2]$ -mediated activation of simple terminal alkynes toward external OH and NH nucleophiles.^[14] A plausible mechanism is given in Scheme 4.

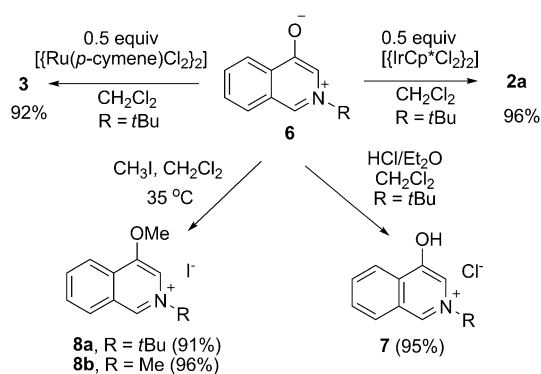


Scheme 4. Proposed catalytic cycle for the synthesis of azomethines.

Upon coordination, the alkyne unit undergoes attack by the nitron group in *six-exo-dig* selectivity (step a). Subsequent N–O cleavage generates an α -oxo carbenoid intermediate (step b). Attack of the amine group at this electrophilic carbene affords a C-bound azomethine complex (step c), and C-bound to O-bound isomerization furnishes intermediate $[\text{D}_1]\text{-2a}$ (step d; $\text{R} = t\text{Bu}$). The catalytic cycle is completed when the azomethine ligand (either C bound or O bound) is substituted by an incoming nitron alkyne substrate.

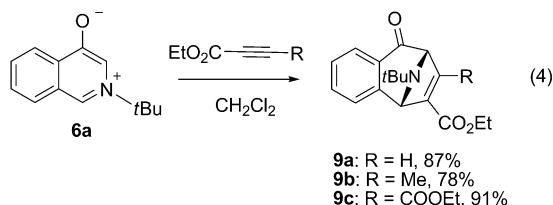
The reactivity of azomethine ylides at the oxygen center has been explored. Stirring a CH_2Cl_2 solution of azomethine **6a** and metal complexes $[\{\text{IrCp}^*\text{Cl}_2\}_2]$ and $[\{\text{Ru}(p\text{-cymene})\text{Cl}_2\}_2]$ (0.5 equiv) resulted in nearly quantitative formation of complex **2a** and **3**, respectively (Scheme 5). However, no coordination occurred when $[\{\text{RhCp}^*\text{Cl}_2\}_2]$ and $[\{\text{Ir}(\text{cod})\text{Cl}\}_2]$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) were used. These results indicated the donor capacity of azomethines is sufficient to substitute bridging chlorides, but binding is limited to rather electrophilic metals. Furthermore, the nucleophilicity of the O atom of azomethines was revealed in the reaction of **6a** with HCl and MeI, wherein protonation and methylation products were isolated, respectively, in high yields (Scheme 5).

Generic azomethines are known to undergo $[3+2]$ dipolar addition with π bonds, thus representing a powerful method for the construction of complex azacycles.^[15] Independently, the groups of Shin^[3b] and Liu^[5b] have reported that gold



Scheme 5. Reactivity of azomethines.

azomethines and analogues, generated from gold-mediated cyclization of nitrone- and nitro alkynes, can undergo intramolecular dipolar addition with alkenes to afford azacycles.^[3b] In these reports, the dipolar addition process is proposed to occur only at the stage of gold-ligated azomethines or analogues. In our studies, azomethine **2a**, either obtained after chromatographic purification or generated in situ under iridium(III) catalysis, reacted smoothly with activated alkynes in an intermolecular fashion, indicating that metal mediation is unnecessary.^[16] Thus tricyclic azacycles **9a–c** were readily isolated in high yield when activated alkynes were used as a coupling partner [Eq. (4)]. In contrast, no reaction occurred when less-reactive alkynes such as $\text{PhC}\equiv\text{CMe}$ were used. The



regioselectivity of this reaction has been confirmed for **9a** by NOE spectroscopy.

The scope of the dipolar addition partners for azomethines was extended to electron-poor olefins such as *N*-methylmaleimide. Eventhough all the azomethines examined undergo [3+2] addition at room temperature (Table 1), those bearing electron-donating groups tend to react more slowly (entries 2 and 4), which is consistent with gold(I)-catalyzed cyclization of nitro alkynes.^[5b] The stereoselectivity of this reaction is substrate dependent. In the case of *N*-*t*Bu-substituted azomethines, the *endo* addition product is consistently isolated as the only isomer (*endo*-**10a–d**), whereas both the *endo* and *exo* addition products were isolated when *N*-benzyl- or *N*-methyl-substituted azomethines were used (entries 5–8). The stereoselectivity was additionally fine tuned for *N*-benzyl azomethines by using the electronic effect of the substituent on the aryl ring.

Table 1: [3+2] Dipolar addition of azomethines with olefins^[a]

Entry	1	Olefin	Product ^[b]
1			$\text{R}^2 = \text{R}^3 = \text{H}$; <i>endo</i> - 10a , 85 %
2			$\text{R}^2 = \text{OMe}$, $\text{R}^3 = \text{H}$; <i>endo</i> - 10b , 42 %
3			$\text{R}^2 = \text{F}$, $\text{R}^3 = \text{H}$; <i>endo</i> - 10c , 68 %
4			$\text{R}^2 = \text{R}^3 = -\text{OCH}_2\text{O}$; <i>endo</i> - 10d , 61 %
5			
6			$\text{R}^2 = \text{H}$; <i>exo</i> - 10e , 20 %
7			$\text{R}^2 = \text{F}$; <i>exo</i> - 10f , 60 %
8			$\text{R}^2 = \text{OMe}$; <i>exo</i> - 10g , 26 %
9			
10			$\text{R}^2 = \text{H}$; <i>exo</i> - 10h , 22 %
11			$\text{R}^2 = \text{OMe}$; <i>exo</i> - 10i , 45 %
12			
13			$\text{R}^2 = \text{H}$; <i>exo</i> - 10j , 42 %
14			$\text{R}^2 = \text{OMe}$; <i>exo</i> - 10k , 32 %
15			$\text{R}^2 = \text{F}$; <i>exo</i> - 10l , 32 %
16			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10m , 32 %
17			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10n , 32 %
18			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10o , 32 %
19			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10p , 32 %
20			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10q , 32 %
21			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10r , 32 %
22			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10s , 32 %
23			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10t , 32 %
24			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10u , 32 %
25			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10v , 32 %
26			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10w , 32 %
27			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10x , 32 %
28			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10y , 32 %
29			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10z , 32 %
30			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10aa , 32 %
31			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ab , 32 %
32			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ac , 32 %
33			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ad , 32 %
34			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ae , 32 %
35			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10af , 32 %
36			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ag , 32 %
37			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ah , 32 %
38			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ai , 32 %
39			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10aj , 32 %
40			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ak , 32 %
41			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10al , 32 %
42			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10am , 32 %
43			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10an , 32 %
44			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ao , 32 %
45			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ap , 32 %
46			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10aq , 32 %
47			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ar , 32 %
48			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10as , 32 %
49			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10at , 32 %
50			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10au , 32 %
51			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10av , 32 %
52			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10aw , 32 %
53			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ax , 32 %
54			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ay , 32 %
55			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10az , 32 %
56			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ba , 32 %
57			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bb , 32 %
58			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bc , 32 %
59			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bd , 32 %
60			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10be , 32 %
61			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bf , 32 %
62			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bg , 32 %
63			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bh , 32 %
64			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bi , 32 %
65			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bj , 32 %
66			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bk , 32 %
67			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bl , 32 %
68			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bm , 32 %
69			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bn , 32 %
70			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bo , 32 %
71			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bp , 32 %
72			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bq , 32 %
73			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10br , 32 %
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75			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bt , 32 %
76			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bu , 32 %
77			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bv , 32 %
78			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bw , 32 %
79			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bx , 32 %
80			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10by , 32 %
81			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10bz , 32 %
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91			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cj , 32 %
92			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ck , 32 %
93			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cl , 32 %
94			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cm , 32 %
95			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cn , 32 %
96			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10co , 32 %
97			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cp , 32 %
98			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cq , 32 %
99			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cr , 32 %
100			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cs , 32 %
101			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ct , 32 %
102			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cu , 32 %
103			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cv , 32 %
104			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cw , 32 %
105			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cx , 32 %
106			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cy , 32 %
107			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10cz , 32 %
108			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10da , 32 %
109			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10db , 32 %
110			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dc , 32 %
111			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dd , 32 %
112			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10de , 32 %
113			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10df , 32 %
114			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dg , 32 %
115			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dh , 32 %
116			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10di , 32 %
117			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dj , 32 %
118			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dk , 32 %
119			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dl , 32 %
120			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dm , 32 %
121			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dn , 32 %
122			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10do , 32 %
123			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dp , 32 %
124			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dq , 32 %
125			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dr , 32 %
126			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ds , 32 %
127			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dt , 32 %
128			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10du , 32 %
129			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dv , 32 %
130			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dw , 32 %
131			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dx , 32 %
132			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dy , 32 %
133			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10dz , 32 %
134			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ea , 32 %
135			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eb , 32 %
136			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ec , 32 %
137			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ed , 32 %
138			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ee , 32 %
139			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ef , 32 %
140			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eg , 32 %
141			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eh , 32 %
142			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ei , 32 %
143			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ej , 32 %
144			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ek , 32 %
145			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10el , 32 %
146			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10em , 32 %
147			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10en , 32 %
148			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eo , 32 %
149			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ep , 32 %
150			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eq , 32 %
151			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10er , 32 %
152			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10es , 32 %
153			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10et , 32 %
154			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10eu , 32 %
155			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ev , 32 %
156			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ew , 32 %
157			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ex , 32 %
158			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ey , 32 %
159			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ez , 32 %
160			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fa , 32 %
161			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fb , 32 %
162			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fc , 32 %
163			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fd , 32 %
164			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fe , 32 %
165			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ff , 32 %
166			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fg , 32 %
167			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fh , 32 %
168			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fi , 32 %
169			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fj , 32 %
170			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fk , 32 %
171			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fl , 32 %
172			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fm , 32 %
173			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fn , 32 %
174			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fo , 32 %
175			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fp , 32 %
176			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fq , 32 %
177			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fr , 32 %
178			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fs , 32 %
179			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ft , 32 %
180			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fu , 32 %
181			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fv , 32 %
182			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fw , 32 %
183			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fx , 32 %
184			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fy , 32 %
185			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10fz , 32 %
186			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ga , 32 %
187			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10gb , 32 %
188			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10gc , 32 %
189			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10gd , 32 %
190			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10ge , 32 %
191			$\text{R}^2 = \text{COOEt}$; <i>exo</i> - 10gf , 32 %
192			$\text{R}^2 = \text{COOEt}$; <i>exo</i>

protons (NCH-CH) are nearly orthogonal in the exo addition products (these two protons are in trans orientation with respect to the newly formed ring); consequently weak coupling and singlet signals were detected in the ^1H NMR spectra. In contrast, well-behaved doublets ($J = 6.5 - 8.5$ Hz) were observed for these protons in the ^1H NMR spectra of the endo addition products.

Other alkenes were employed to additionally define the scope of dipolar addition with **6a** generated in situ. When ethyl acrylate was employed (entry 9), four addition products were obtained as a result of different regio- and stereochemistries. Two endo addition products and two exo addition products were isolated as a mixture of two regioisomers, indicating the low selectivity of this reaction. The addition readily occurred for *trans*-EtO₂CH=CHCO₂Et at room temperature to give **12** as the only isomeric product, the structure of which was elucidated on the basis of ^1H NMR and NOE spectroscopy. This [3+2] cycloaddition is highly stereospecific and the observed product indicates that the endo interaction between the iminium moiety and the ester group in the transition state plays a dominant role. In sharp contrast, a slow reaction (60 °C, 3 days) was observed for *cis*-EtO₂CH=CHCO₂Et, and two stereoisomeric products were isolated in 57 % total yield in a 3.8 (exo):1 (endo) ratio. The observed low reactivity might be attributed to the increased steric hindrance, among other factors.

In summary, we have achieved the internal redox cyclization of nitron-functionalized terminal alkynes mediated by a simple iridium(III) complex in both stoichiometric and catalytic reactions. These reactions occurred selectively to result in the isolation of unusual azomethine ylides. Rare iridium O-bound azomethine complexes have been isolated and characterized, and show a rather short C–O distance in the azomethine unit. Catalytic cyclization of nitron alkynes under mild reaction conditions afforded azomethine ylides that have been successfully isolated for the first time. Reactivity of the azomethine ylides and their complexes towards electrophiles and unsaturated molecules has been demonstrated. In particular, azomethine ylides can undergo an intermolecular [3+2] dipolar addition reaction with activated alkynes and alkenes. Different stereoselectivities have been observed in the dipolar addition of alkenes as a result of substrate control. Additional studies on the intrinsic aspects of such reactive intermediates are under way for the development of other synthetic methodologies.

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