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Cycloadditions

Iridium Catalyzed Carbocyclizations: Efficient (5+2) Cycloadditions of Vinylcyclopropanes and Alkynes

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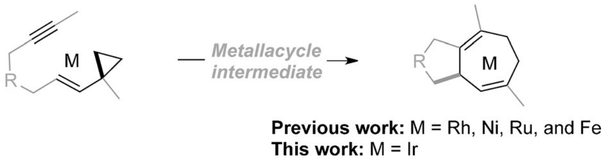
Abstract: Third-row transition metal catalysts remain a largely untapped resource in cycloaddition reactions for the formation of medium-sized rings. Herein, we report the first examples of iridium-catalyzed inter- and intramolecular vinylcyclopropane (VCP)–alkyne (5+2) cycloadditions. DFT modeling suggests that catalysis by iridium(I) proceeds through a mechanism similar to that previously reported for rhodium(I)-catalyzed VCP–alkyne cycloadditions, but a smaller free energy span for iridium enables substantially faster catalysis under favorable conditions. The system is characterized by up to quantitative yields and is amenable to an array of disubstituted alkynes and vinylcyclopropanes.

Metal-catalyzed cycloadditions constitute a unique platform for assembling high-value cyclic products from simple components. Formation of seven-membered carbocycles from vinylcyclopropanes (VCPs) and alkynes catalyzed by rhodium serves as an illustration. First reported by Wender in 1995,[1] this process has enabled streamlining complex molecule syntheses[2] and provided a mechanistic basis for developing new reactions including higher order cycloadditions[3] and (5+2) reactions with other 2π components.[4] Intramolecular versions catalyzed by ruthenium,[5] nickel,[6] and iron[7] have been reported, but the intermolecular reaction that benefits from simple and often commercially available substrates has remained exclusive to rhodium catalysis.[8] A remaining challenge towards improving the efficiency and cost, as well as providing new mechanistic opportunities for interception of intermediates, is the introduction of third-row transition metals as catalysts in this context.[9]



To this end, we envisioned that comparatively inexpensive iridium would be a suitable candidate.[10] Strong interactions between carbon and iridium suggest that appropriate iridium-based systems would combine a propensity for facile oxidative cyclometalation of VCPs with a favored insertion of π-components into the resulting metallacycles;[11a] both likely prerequisites for efficient catalysis with less activated substrates.[11b,c] Herein, we report that cationic iridium complexes with cyclooctadiene (cod)[12a,b] or dibenzo[*a*,*e*]cyclooctatetraene (dbcot)[12c] ligands are exceptionally efficient catalysts for inter- and intramolecular (5+2) cycloadditions between VCPs and disubstituted alkynes. Comparative studies show rates of catalysis 50 times or higher compared to those of analogous rhodium complexes in intermolecular reactions. Density functional theory (DFT) calculations suggest that a small free energy span in the catalytic cycle for iridium accounts for this difference. Iridium catalysis is moreover shown to be compatible with a variety of functional groups with up to quantitative yields.

At the outset, we explored the use of a cationic iridium(I) catalyst formed in situ from commercially available [{Ir(cod)Cl}$_2$] and AgPF$_6$ for the reaction between 4-octyne[13] and commercially available VCP **1a** (Table 1).[14]

In a mixture of 1,2-dichloroethane (DCE)/2,2,2-trifluoroethanol (TFE)[15] as solvent (9:1 v/v), the reaction worked remarkably well to give cycloadduct **3a** in an essentially quantitative yield in under two minutes at ambient temperature (Table 1, entry 1). Varying the reaction conditions revealed that [{Ir(cod)Cl}$_2$] did not catalyze the reaction without removal of the chloride (Table 1, entry 3). A slower reaction with tetrakis(3,5-trifluoromethyl)phenyl borate (BAr$_F$$^-$) as the counter ion is likely a reflection of a less efficient counter ion metathesis due to a limited solubility of NaBAr$_F$ in DCE (Table 1, entry 4). With [{Ir(cod)Cl}$_2$] as the precatalyst, 1.25 mol% was necessary to preserve a high turnover rate throughout the reaction (Table 1, entry 5).[16] Exchange of the cod ligand in precatalyst **2a** for a more tightly coordinated dbcot ligand[17] in **2b** enabled a preserved turnover rate using only 0.7 mol% of precatalyst (Table 1, entries 6 and 7). A simplified protocol using a well-defined cationic η^6-arene iridium complex, [(cod)Ir(C$_{10}$H$_8$)]SbF$_6$ (**2c**),[12a,b,18] was also investigated. This complex gave a complete conversion of the starting material within 15 min and a 98% yield of **3a** after hydrolysis (Table 1, entry 8). With some effort, single crystals of **2c** were also obtained from which the solid phase structure was solved (Table 1; see the Supporting Information for details).[19] To our knowledge, this represents the first XRD structure of a cationic η^6-arene iridium–cod complex. Although air stable in the crystalline form,

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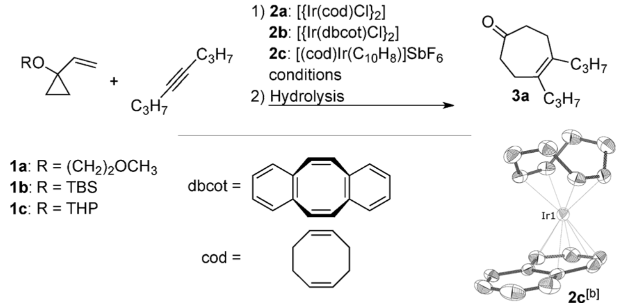
Table 1. Optimization of the intermolecular (5 + 2) reaction.[a]



Entry	VCP	(Pre-)Catalyst (mol %)	Additive (mol %)	Time	Solvent	Yield [%][c]
1	**1 a**	**2 a** (2.5)	$AgPF_6$ (8)	2 min	DCE/TFE	99[d]
2	**1 a**	**2 a** (2.5)	$AgPF_6$ (8)	5 min	DCE/HFIP[e]	95
3	**1 a**	**2 a** (2.5)	–	24 h	DCE/TFE	–
4	**1 a**	**2 a** (2.5)	$NaBAr_F$ (8)	90 min	DCE/TFE	99
5	**1 a**	**2 a** (1.25)	$AgPF_6$ (4)	5 min	DCE/TFE	95
6	**1 a**	**2 b** (1.25)	$AgPF_6$ (4)	5 min	DCE/TFE	98
7	**1 a**	**2 b** (0.7)	$AgPF_6$ (2)	30 min	DCE/TFE	96
8	**1 a**	**2 c** (5.0)	–	< 15 min	DCE/TFE	98
9	**1 b**	**2 a**(2.5)	$AgPF_6$ (8)	4 h	DCE/TFE	31
10	**1 c**	**2 a** (2.5)	$AgPF_6$ (8)	5 h	DCETFE	53[d]
11	**1 a**	**2 a** (2.5)	$AgPF_6$ (8)	30 min	Me-THF/TFE	96
12	**1 a**	**2 a** (2.5)	$AgPF_6$ (8)	180 min	Me-THF	77
13	**1 a**	**2 a** (2.5)	$AgPF_6$ (8)	20 min	PC/TFE	83[d]

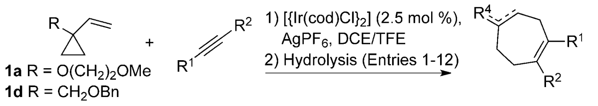
[a] Procedure: To a solution of **2 a/b/c** (up to 16 mM) in the solvent or solvent mixture indicated (9:1 v/v co-solvent) was added VCP (1.0 equiv) and alkyne (1.2 equiv) followed by the additive (if applicable). After consumption of the VCP (TLC control), or no observable change in reaction progress, the mixture was subjected to acidic hydrolysis; [b] thermal ellipsoids drawn at 30% probability. Hydrogen atoms and the SbF_6^- counter ion are omitted for clarity; [c] determined by ^1H NMR spectroscopy of the crude reaction mixture using 1-methoxynaphthalene as internal standard; [d] yields of isolated product; [e] 1,1,1,3,3,3-hexafluoro-isopropanol.

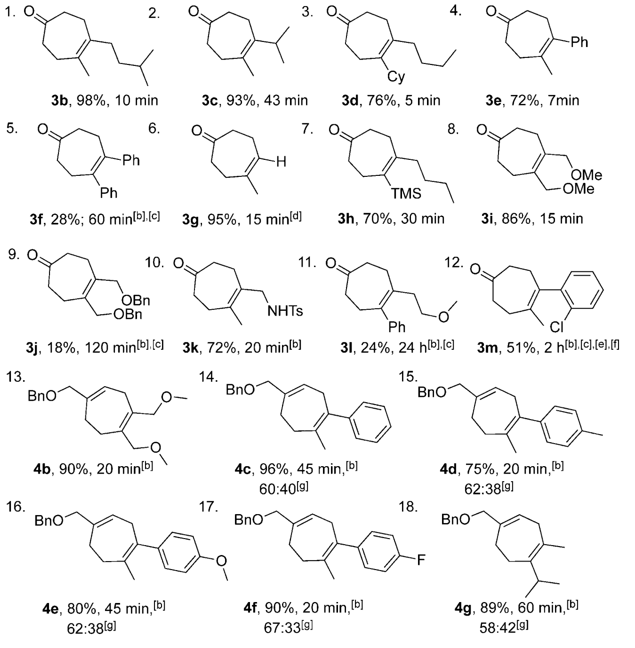
amorphous **2 c** was susceptible to aging, explaining why in situ preparation of the active species from [{Ir(L)Cl}$_2$] precursors generally gave superior results in catalysis. When using DCE as the solvent, addition of fluorinated co-solvents was necessary to retain high yields and reaction rates (not shown).[20] Importantly, nonchlorinated solvents, such as 2-Me-THF (with or without TFE added) and propylene carbonate (PC),[21] also allowed for efficient catalysis (Table 1, entries 11–13).

The mechanism and selectivity of rhodium-[22] and ruthenium[23]-catalyzed (5 + 2) reactions have been extensively studied. For insight into the iridium(I)-catalyzed process, the reaction between 2-butyne and 1-methoxy-1-vinyl cyclopropane catalyzed by [Ir(cod)]$^+$ was explored by DFT using the m06-2x functional and the LACVP** basis set (Figure 1).[24] The lowest energy pathway found originated with an oxidative cyclometalation of the VCP–Ir complex **I1**$_{\mathbf{Ir}}$ to form metallacyclohexene **I2**$_{\mathbf{Ir}}$. An alternative mechanism initiated with an ene–yne cyclometalation of **I1**$'_{\mathbf{Ir}}$ was discarded based on the comparatively high activation barrier for this process (**I1**$'_{\mathbf{Ir}}$-**TS1**$'_{\mathbf{Ir}}$ = 26.95 kcal mol^{-1}). As catalysis by iridium(I) shares the principal elements of the mechanism previously invoked for rhodium(I), the energy profile for the analogous reaction catalyzed by [Rh(cod)]$^+$ was also calculated for comparison. Despite an apparent similarity between the two pathways, several distinguishing features can be highlighted. Formation of both **I2** and **I3** in this system is *exergonic* for iridium whereas the corresponding processes are marginally *endergonic* for rhodium. The migratory insertion barrier is more favorable with iridium, whereas reductive elimination is more facile for rhodium. The largest activation barrier between a transition state and a preceding intermediate is approximately 16 kcal mol^{-1} for both metals. The energy surface for iridium catalysis is however noticeably more level and the turnover frequency determining transition state and intermediate are not the same in the two cycles.[25] As a consequence, the free energy span (δ*E*), suggested to be proportional to the rate of catalysis,[26] is only 16.03 kcal mol^{-1} for iridium (**I4**$_{\mathbf{Ir}}$→**TS3**$_{\mathbf{Ir}}$) compared to 28.22 kcal mol^{-1} for rhodium (**I5**$_{\mathbf{Rh}}$→**TS2**$_{\mathbf{Rh}}$), which implies that catalysis by cationic iridium(I) would be comparatively fast under favorable conditions.

Motivated by this prediction, the relative rates of catalysis with a less-reactive 5C component, VCP **1 d**,[27] were investigated in a comparative study between [Ir(cod)]$^+$, [Ir(dbcot)]$^+$, and their analogous rhodium complexes (Figure 2). [Ir(dbcot)]$^+$

Table 2. Intermolecular (5 + 2) reactions; substrate scope.[a]





1. **3b**, 98%, 10 min
2. **3c**, 93%, 43 min
3. **3d**, 76%, 5 min
4. **3e**, 72%, 7min
5. **3f**, 28%; 60 min[b],[c]
6. **3g**, 95%, 15 min[d]
7. **3h**, 70%, 30 min
8. **3i**, 86%, 15 min
9. **3j**, 18%, 120 min[b],[c]
10. **3k**, 72%, 20 min[b]
11. **3l**, 24%, 24 h[b],[c]
12. **3m**, 51%, 2 h[b],[c],[e],[f]
13. **4b**, 90%, 20 min[b]
14. **4c**, 96%, 45 min,[b] 60:40[g]
15. **4d**, 75%, 20 min,[b] 62:38[g]
16. **4e**, 80%, 45 min,[b] 62:38[g]
17. **4f**, 90%, 20 min,[b] 67:33[g]
18. **4g**, 89%, 60 min,[b] 58:42[g]

[a] Yields of isolated product are given unless otherwise stated; [b] [{Ir(dbcot)Cl}$_2$] was used; [c] 5.0 mol % precatalyst used; d] 1-trimethylsilylpropyne was used as the alkyne component; [e] yield determined by ^1H NMR spectroscopy of the crude reaction mixture using 1-methoxynaphtalene as internal standard; [f] HFIP was used; [g] ratio of regioisomers measured by ^1H NMR spectroscopy of the crude reaction mixture. Major regioisomer is shown.

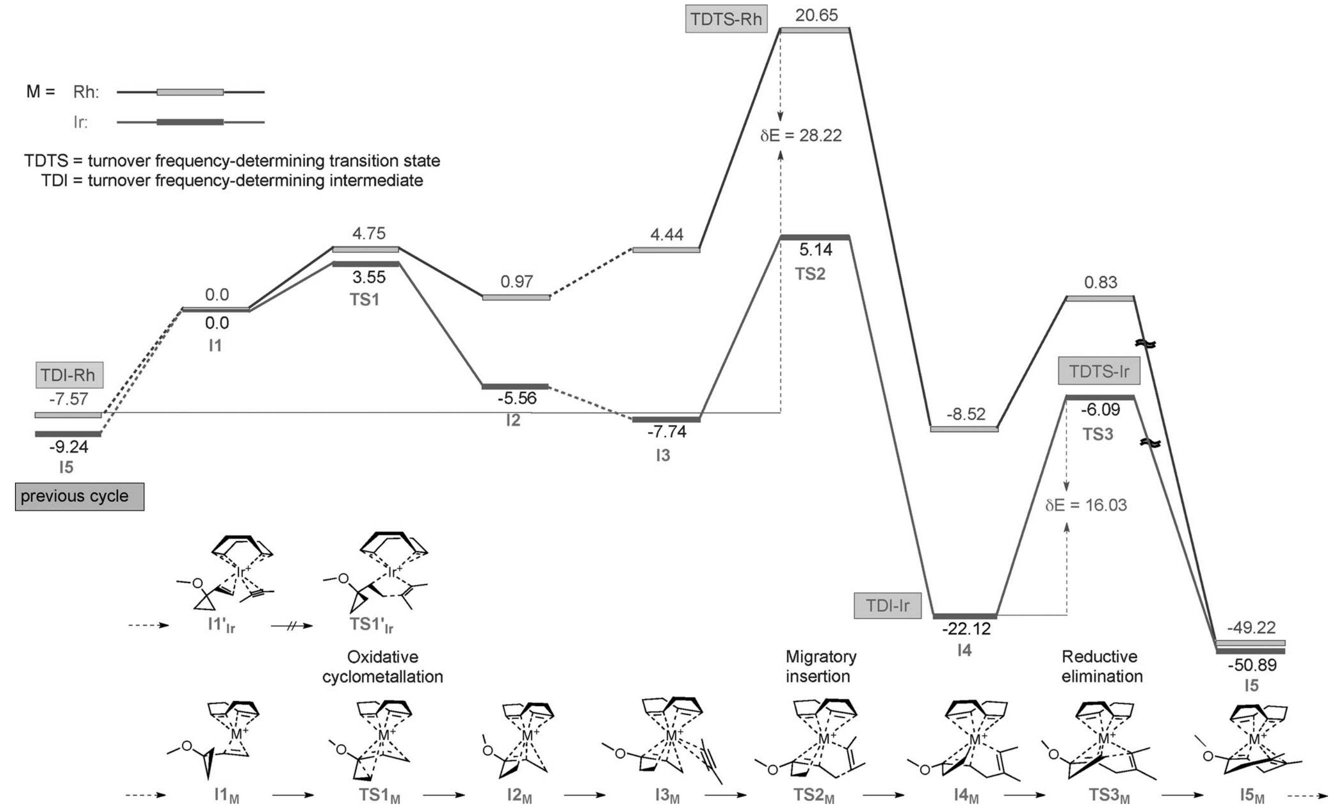


Figure 1. Free energy surfaces for the $[Ir(cod)]^+$- and $[Rh(cod)]^+$-catalyzed (5+2) cycloadditions between 1-methoxy-1-vinyl cyclopropane and 2-butyne. Energies are given in $kcal\,mol^{-1}$.

gave the fastest conversion in the series and reached completion within four minutes under the conditions studied. The turnover frequency (observed) of $10.0\ min^{-1}$ for this catalyst was seven times higher than for $[Ir(cod)]^+$ ($1.3\ min^{-1}$) and 50 times higher than for $[Rh(dbcot)]^+$ ($0.2\ min^{-1}$).[28]

With respect to substrate tolerance, a broad range of alkynes competently participates in the (5+2) reaction with VCPs **1a** and **1d** under iridium catalysis (Table 2). Noteworthy examples include 1-silylalkynes that can function as synthetic equivalents of terminal alkynes via protodesilylation of the cycloadduct during the workup, or to give vinylsilane products (Table 2, entries 6–7). Of utility for synthetic applications is also the participation of aryl halide-substituted alkynes, as exemplified by formation of aryl chloride **3m** (Table 2, entry 12). Sulfonamide and ether substituents are well tolerated in the reaction. However, the precise nature and position of basic groups on the alkyne component will in some cases give reduced efficiency (Table 2, entries 8–11). For more challenging substrate combinations, the use of $[\{Ir(dbcot)Cl\}_2]$ as the precatalyst and/or a higher catalyst load generally provided superior results. Replacing TFE by HFIP as co-solvent avoided the formation of stable ketals, which were formed from the intermediate enol ethers with TFE in some reactions. In reactions between VCP **1d** and unsymmetrical aryl-methyl substituted alkynes, a slight preference for insertion of the alkyne with the aryl group distal to the metal was seen (Table 2, entries 13–17). Varying the electronic properties of the aryl group had only marginal influence on this selectivity. In contrast, insertion of an isopropyl-methyl-substituted alkyne showed a modest preference for insertion of the larger isopropyl moiety proximal to the metal (Table 2, entry 18).

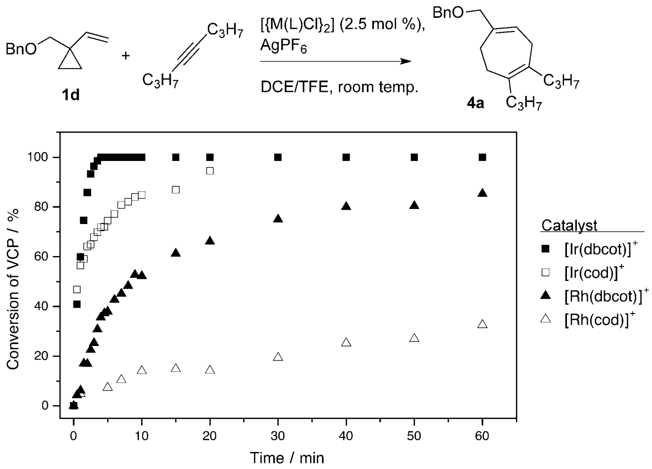
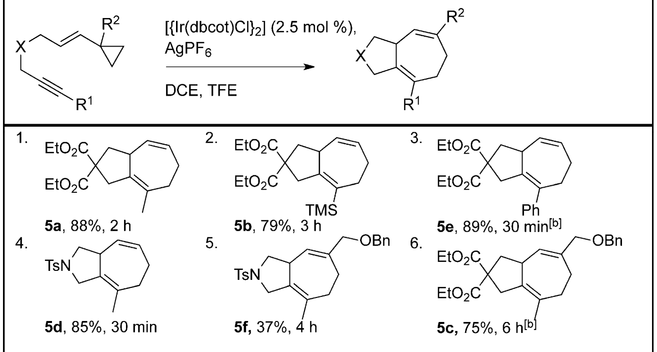


Figure 2. Kinetic comparison of iridium and rhodium catalysis.

The conditions developed for intermolecular (5+2) reactions with iridium extended also to efficient intramolecular reactions with tethered VCPs and alkynes (Table 3).

The best results were again obtained using $[\{Ir(dbcot)Cl\}_2]$ as the precatalyst. Substrates in which the VCP is not pre-organ-

Table 3. Intramolecular (5 + 2) reactions: Substrate scope.[a]



1. **5a**, 88%, 2 h
2. **5b**, 79%, 3 h
3. **5e**, 89%, 30 min[b]
4. **5d**, 85%, 30 min
5. **5f**, 37%, 4 h
6. **5c**, 75%, 6 h[b]

[a] Yields of isolated product are given; [b] 5 mol% precatalyst used.

ized by substitution at the C1 position of the cyclopropane[21c] reacted efficiently at ambient temperature to give a series of diversely functionalized fused bicyclic products in good yields (Table 3, entries 1–4).

In summary, the first examples of iridium-catalyzed (5 + 2) cycloadditions are presented. The system is characterized by rapid catalysis and up to quantitative yields. In a comparative study of intermolecular (5 + 2) reactions, previously restricted to rhodium catalysis, iridium showed rates of catalysis 50 times higher or more compared to those of structurally analogous rhodium salts. DFT calculations suggested that this difference originates from a surprisingly level free-energy surface in iridium catalysis, which is a reflection of facile cyclometalation and insertion steps in the catalytic cycle. The conditions presented are amenable to both inter- and intramolecular reactions and compatible with a range of functional groups. Further synthetic and mechanistic studies based on this system are currently under way.

Acknowledgements

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Keywords: cycloadditions · density functional calculations · homogeneous catalysis · iridium · seven-membered rings

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[28] The conversion of VCP was quantified by GC using naphthalene as internal standard. Each data point is the average of three independent experiments. See the Supporting Information for details.

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COMMUNICATION

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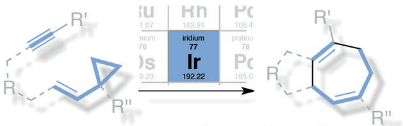

– inter- and intramolecular
– 28 examples
– up to 99% yield
– down to < 2 min reaction time

Third row's a charm: Efficient inter- and intramolecular vinylcyclopropane–alkyne (5+2) cycloadditions catalyzed by iridium(I) are presented. Density functional calculations suggest that catalysis by iridium(I) proceeds through a mechanism similar to the established rhodium(I)-catalyzed method, but a smaller free energy span for iridium enables substantially faster catalysis under favorable conditions (see scheme).