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ARTICLE

Challenges in Cyclometalation: Steric Effects Leading to Competing Pathways and η^1,η^2-Cyclometalated Iridium(III) Complexes

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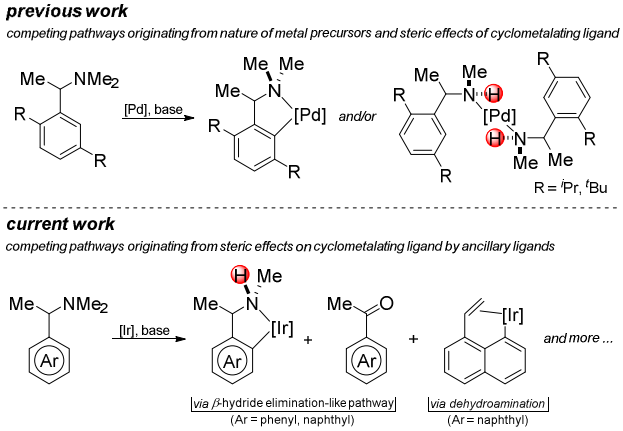
Houguang Jeremy Chen,[a] Ronald Hong Xiang Teo,[a] Jonathan Wong,[a] Yongxin Li,[a] Sumod A. Pullarkat[a] and Pak-Hing Leung*[a]

The iridation of (R)-N,N-dimethyl-1-(1-naphthyl)ethylamine in the presence of base afforded an assortment of products ranging from organic molecules to coordinated systems and cyclometalated complexes. The transformation affirmed the postulation where steric effects within the coordination sphere favors a β-hydride elimination-like decomposition pathway, competing alongside ortho-metalation, thus leading to iminium intermediates. The same procedure also generated an unprecedented carbocyclic η^1,η^2-cycloiridated species that could not be attained from the direct cyclometalation of its organic ligand.

Introduction

The evolution of cyclometalation from an endeavor into new coordination modes to its modern stance into applications has brought forth its compounds to the forefront of research. Cyclometalated complexes can serve as potent catalysts,[1] auxiliaries,[2] photo-luminescing agents[3] and biotherapeutic drugs,[4] and its concepts can be applied to obtain an extensive assortment of compounds through C–H bond functionalization protocols as reactive intermediates.[5]

Generally, the principles of cyclometalation revolve about the electronic nature of both the metal center and the donor, as well as steric factors along the projected organometallic ring system.[6] Previously, we uncovered an undocumented consequence of unsuccessful cyclometalation where a competing pathway competed against the former procedure.[7] We had postulated that the latter process involved reactive iminium intermediates which, for the first time, we were able to provide experimental evidence to affirm our hypothesis. The article also extends the phenomenon to complexes beyond palladium (in this case, iridium) and steric factors about the coordination sphere (instead of the cyclometalating ligand). Additionally, we were able to isolate an unprecedented carbocyclic alkene-type η^1,η^2-cycloiridated complex, with its olefinic π-electrons coordinatively bonded to the metal center.



Scheme 1. Schematic representation of previous and current works in competing pathways of cyclometalation.

While the field of cyclometalation has been recognized as one of the most explored areas within organometallic chemistry,[6a,8] the process leading to alternative pathways is not well-defined since its prevalence is uncommon (and/or likely to be overlooked or undocumented). A quick review of literature depicted some of these protocols to be simplified as oxidation processes to their respective products.[9] Moreover, the mode of activation to access vinyl-derived cyclometalated species has not been reported. With the interest to understand the chemistry behind these reactions, our intentions were to investigate the origins and mechanistic pathways to these compounds. More importantly, with the advent of catalytic C–H bond functionalization reactions becoming a mainstream research area,[10] the work could serve

[a] *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore.*
[*] Corresponding author: P.-H. Leung *(pakhing@ntu.edu.sg)*

†Electronic Supplementary Information (ESI) available. CCDC 1815863 ((*R*C,*R*N,*S*Ir)-**1**), 1830655 (*rac*-**5**) and 1815864 (*rac*-**9**). For ESI and crystallographic data in electronic format, please see DOI: 10.1039/x0xx00000x

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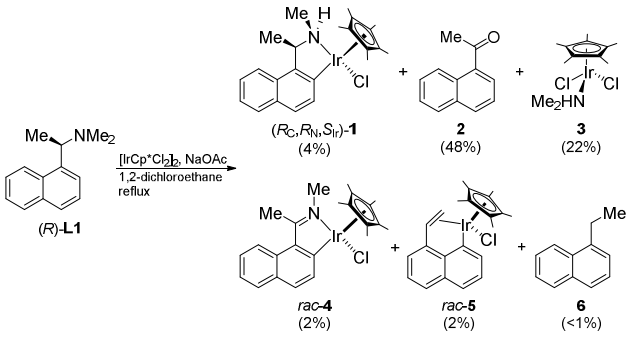
as a reference to byproducts and/or new modes of activation to access synthetically-useful chemicals.

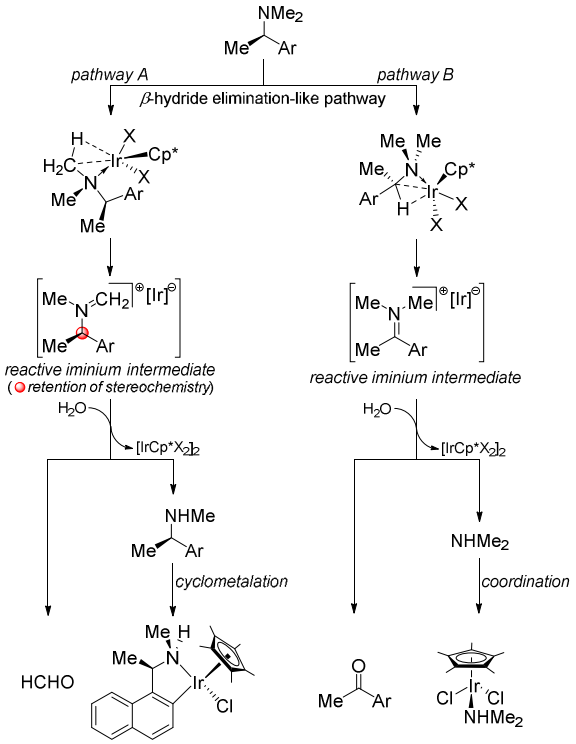
Results and Discussion

The iridation of optically-active (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (*R*)-**L1** with $[IrCp^*Cl_2]_2$ in the presence of NaOAc at elevated temperatures afforded six isolable compounds – four coordinated species, three of which were cyclometalated, and two organic molecules (Scheme 2). Among these compounds were *ortho*-iridated *N*-demethylated complex (R_C,R_N,S_{Ir})-**1**, 1-acetonaphthone **2** and coordinated dimethylamine complex **3** which corresponded to products expected from the postulated competing pathway. The remaining three compounds, namely, cycloiridated imine-derived complex *rac*-**4**, carbocyclic cyclometalated species *rac*-**5** and 1-ethylnaphthalene **6**, were not observed in our prior studies.[7] It should also be noted that the same procedure did not proceed when conducted at ambient temperature. Lastly, while the reaction proceeded in the absence of external base, longer reaction time was required to attain the products in comparable quantities.



Scheme 2. The iridation reaction of (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (*R*)-**L1**.[11]

The formation of the former three products can be derived from a *β*-hydride elimination-like process ("the competing pathway"). The abstraction of the hydrogen atom by the base, assisted by agostic C–H bond activation, produced a reactive iminium intermediate that can be readily hydrolyzed to provide the said products, albeit the absence of formaldehyde, possibly due to its volatility in the heated mixture (Scheme 3). The mechanism was supported by the retention of stereochemistry at the α-carbon in iridacycle (R_C,R_N,S_{Ir})-**1** along Pathway A which emphasized the lack of involvement of the acidic α-proton within the mechanism. Similarly, deuterium labelling studies (with the proton at the α-carbon in the racemic ligand replaced by deuterium) mirrored comparable experimental observations with its corresponding complex d_1-*rac*-**1** isolated in similar deuteration levels (Scheme 7). The transformation along Pathway B mimicked the iridium(III) intermediates proposed by Stirling,[12] although hydrolysis of the iminium derivative was observed under our reaction conditions. Likewise, its palladium counterpart was suggested in several *N*-dealkylation experiments.[13] Whilst efforts were made to conduct the experiment under anhydrous conditions,



we were unsuccessful in isolating the transient species prior to hydrolysis or spectroscopic identification.

Scheme 3. Proposed mechanism for the competing pathway in the iridation procedure (X = Cl, OAc).

It is important to reiterate that the ligand motif is known to cyclometalate well with various metal salts.[14] As such, we can extend the considerations of the competing pathway from the nature of the ligand to steric effects about the coordination sphere. In this instance, the *ortho*-metalation procedure was believed to be impeded by the bulky Cp* spectator ligand. To investigate the extent of its effects on the cyclometalating ligand, we proceeded to expose its corresponding phenyl derivative (*R*)-**L2** and *N*,*N*-dimethyl-1-naphthylmethylamine **L3** to our experimental conditions. The iridation of phenyl-based tertiary amine (*R*)-**L2** (Scheme 4a) returned similar observations to the earlier metalation attempt but with fewer byproducts. This result indicates that the failed cyclometalation attempt was not a consequence of the known spatial interaction between the α-methyl substituent and its neighbouring proton on the aromatic ring within the ligand.[15] The isolation of coordinated dimethylamine complex **3** and acetophenone **7** from the procedure reflects part of the proposed mechanistic pathway of the competing reaction. On the other hand, the *ortho*-iridation of the achiral naphthalene-based isomer **L3** was successful with the procedure providing the desired metallacycle *rac*-**9**, albeit sluggishly at room temperature (Scheme 4b). This sheds light on the possible

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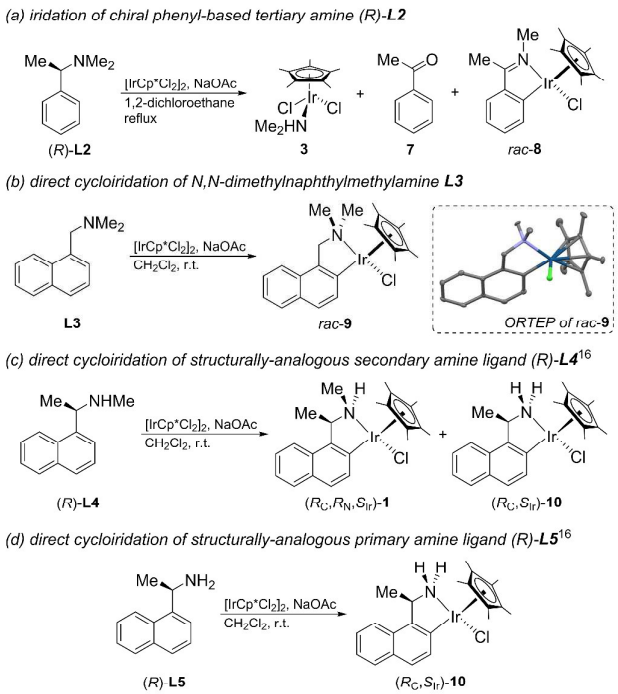
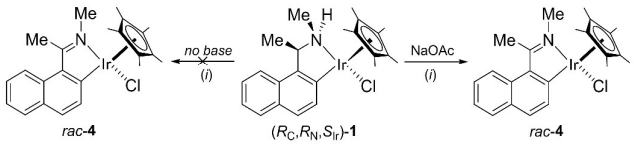
spatial threshold of the protocol where an additional methyl substituent along the projected organometallic ring may have hindered the formation of the cycloiridated complex. The idea was reinforced in a recent work on the direct cycloiridation of optically-active secondary and primary amine ligands (*R*)-**L4** and (*R*)-**L5** respectively.[16] In the former case (Scheme 4c), whilst cyclometalation was the preferred route for the reaction, the protocol retained a preference for the slower competing pathway leading to *N*-demethylated product (R_C,S_{Ir})-**10**. Conversely, its primary derivative, produced solely the same iridacycle with no signs of byproducts (Scheme 4d).



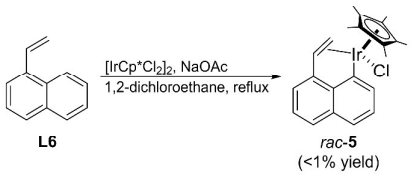
Scheme 4. Experiments for the determination of steric threshold for the competing pathway.

Next, we investigated the formation of imine-type *ortho*-iridated complex *rac*-**4**. Since the demethylation of an *N*-methyl moiety was unlikely, it was suggested that the formation of this compound was derived from complex (R_C,R_N,S_{Ir})-**1** *via* a dehydrogenation procedure. While dehydrogenation of secondary *amino* iridacyclic species is not uncommon,[17] an earlier investigation involving the thermal stability of the same metallacycle revealed that the complex was not oxidized in solution even at elevated temperatures.[16] We predicted that the base may have played a role in the oxidization process. As such, we proceeded to heat the solvated complex in the presence of NaOAc. The reaction was sluggish, but generated the imine-based iridacycle, on the basis of its methyl spectroscopic handles at 2.98 and 3.98 ppm in the crude ^{1}H NMR spectrum. It should also be mentioned that the dehydrogenation procedure racemized the stereogenic center at iridium demonstrating the labile nature of the imine coordinate within the coordination sphere.



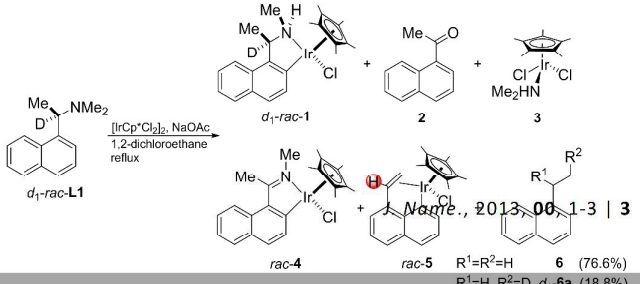
Scheme 5. Experiments on the dehydrogenation of cycloiridated complex (R_C,R_N,S_{Ir})-**1**. Reaction conditions: (*i*) 1,2-dichloroethane, reflux.

Next, we reviewed the carbocyclic olefin-type cycloiridated complex *rac*-**5**. While coordinated olefins are common within organometallic chemistry,[18] cyclometalated variants are scarce and, to the best of our knowledge, have only been synthesized from the rearrangement of olefins and activation of C–H bonds.[19] The current iridation protocol, while unoptimised, presents access to these rare compounds. It was necessary to check that *rac*-**5** was not formed from direct cycloiridation of the olefinic ligand **L6**. 1-vinylnapthalene was subjected to the same reaction conditions and the olefinic complex was only isolated in <1% yield. The poor reactivity could be attributed to the poor directing efficacy of the alkene moiety within the vinylic framework. The experiment also demonstrated the improbability of the iridation of (*R*)-**L1** to produce 1-vinylnaphthalene as an intermediate to give the olefin-directed iridacycle.



Scheme 6. Attempted direct cycloiridation of 1-vinylnaphthalene **L6** to carbocyclic olefin-directed cycloiridated complex *rac*-**5**.

To gain further understanding into its formation, we conducted the same experiment utilizing deuterated ligand d_1-*rac*-**L1** which has its proton at the stereogenic carbon center exchanged with deuterium (Scheme 7). To our surprise, the resultant η^1,η^2-iridacycle did not contain any trace of deuterium on its structure. It was thus intuitive that the dehydroamination procedure involved the deuterium on the α-carbon. With the information at hand, we proposed a mechanism in which the olefin-type metallacycle *rac*-**5** was derived from the dehydroamination of the six-membered amine-directed cycloiridated species (Scheme 8). However, despite numerous attempts, we were unable to physically isolate or spectroscopically detect the intermediate in our experiments.



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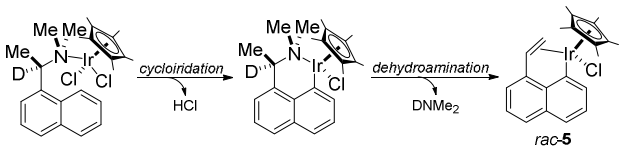
Scheme 7. Deuterium labelling experiment on the iridation of tertiary amine d_1-*rac*-**L1**.



Scheme 8. Proposed mechanism to carbocyclic olefin-directed cycloiridated complex *rac*-**5** *via* complexed cyclic intermediate.

Crystallographically, the isolated yellow block-like complex provided some insights into the coordination mode of the compound. The C=C olefinic bond length (141 pm) within the complex was found to be slightly longer than that to an uncoordinated alkene (134 pm), in line with reported iridium(III) complexes containing coordinated olefins.[20] Along the plane of the naphthalene system, the alkene moiety was found to lie out of the plane by 63.8°, tilting 30.4° off along the Ir–Cl axis. Spectroscopically, the NMR spectra were also in agreement with the crystal structure of the complex. The ^{13}C NMR spectrum depicted the coordinated olefin moiety with its distinctive upfield chemical shifts at 56.16 (ArCH=*C*H$_2$) and

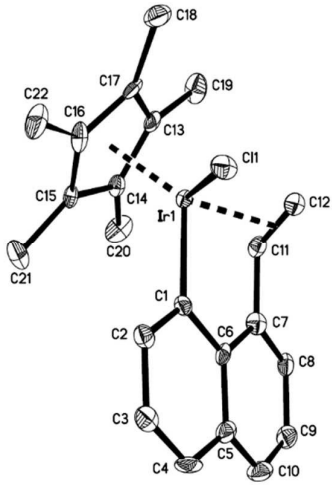
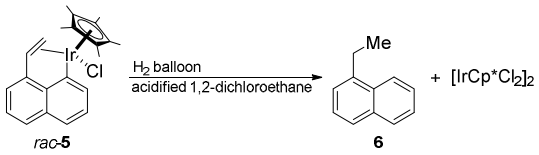


Figure 1. Molecular structure of cycloiridated complex *rac*-**5** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Ir–C_1 (2.050(6) Å), Ir–C_{11} (2.171(7) Å), Ir–C_{12} (2.131(7) Å), Ir–Cl (2.4057(16) Å), C_{11}–C_{12} (1.407(10) Å), C_1–Ir–Cl (83.66(18)°), C_{11}–Ir–C_{12} (38.2(3)°), C_7–C_{11}–C_{12} (122.1(6)°).

80.82 (Ar*C*H=CH$_2$) ppm. Coupling between the olefinic protons in the ^{1}H NMR spectrum were within expected values averaging 8.8 Hz and 11.3 Hz for *cis* and *trans* H–H coupling respectively. Lastly, like its imine counterpart, the alkene-coordinated species returned no optical activity denoting a loss of stereogenic information from its optically-active substrate.

Examining 1-ethylnaphthalene **6**, it can be thought that the compound was a hydrogenated fragment of the ligand framework in the carbocyclic complex. With that in mind, we performed a simple hydrogenation procedure on the complex in acidified 1,2-dichloroethane. Full conversion to the hydrocarbon was observed in the experiment (Scheme 9). We postulated that the source of dihydrogen originate from the dehydrogenation protocol of cycloiridated secondary amine complex (R_C,R_N,S_{Ir})-**1** (Scheme 5). As such, following the hydrogenation process, the monodentate *C*-coordinated species was believed to undergo further protonlysis to provide 1-ethylnaphthalene **6** and [IrCp*Cl$_2$]$_2$. To support this conjecture, we note that the earlier deuterium studies produced two variants of hydrocarbon **6**, namely d_1-**6a** and d_1-**6b**, with the latter having deuterium on the *α*-carbon and the former deuterated at the *β*-carbon. Spectroscopically, the results were particularly intriguing. While we observed the presence of deuterium on both *α*- and *β*-carbon of the organic molecules, deuterium levels were relatively low at 18.8% and 4.6% respectively (compared to 92.5% at the *α*-carbon of ligand d_1-*rac*-**L1** prior to the reaction). The result signified an alternate source of dihydrogen outside our prediction within the reaction mixture. Otherwise, the olefin-based iridacycle could undergo a separate distinct mechanism that adds the hydrogen atoms to its organic framework differently to



produce the hydrocarbon.

Scheme 9. Hydrogenation of carbocyclic olefin-directed cycloiridated complex *rac*-**5** to 1-ethylnaphthalene **6**.

Conclusions

The iridation of tertiary amine (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine (*R*)-**L1** using [IrCp*Cl$_2$]$_2$ revealed the limits of cyclometalation from the viewpoint of the *ortho*-metalating ligand. In this instance, the commonly-known optically-active cyclometalating ligand was unable to cyclize due to the sterically-bulky Cp* spectator ligand that was present on the metal center. This resulted in the less favorable *β*-hydride elimination-like process to take place leading to hydrolyzed products (and consequently its corresponding carbonyl and/or *N*-demethylated compounds) from the reactive iminium species. Whilst the experiment was not chemoselective, the reaction offered evidence into both mechanistic pathways of the competing reaction. It is vital to consider both steric bulk of the substrates and ligands about the metal center when synthesizing cyclometalated systems or performing catalytic C–H bond functionalization protocols. The same concept can also be exploited to access synthetically-challenging or novel secondary amines through the *N*-dealkylation procedures.

Next, the iridation procedure also provided an exclusive access to a rare olefin-directed metallacycle that cannot be synthesized from direct cyclometalation. With the scope of cyclometalated compounds expanded, the carbocyclic complex could exhibit greater potential in novel studies and

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applications. Moreover, the *in-situ* generation of the metallacycle by catalytic means could bring forth new methodologies that add moieties across the C=C olefinic bond, as well as functionalizing the *ipso*-carbon to construct new compounds.

Finally, while much efforts have been placed in the prescribed iridation procedure, we strongly believe that the idea can be applied to metalation protocols of other transition metal elements.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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11 Isolated yields (in parenthesis). It should be noted that the products do not account for all tertiary amine ligand (*R*)-**L1** present in the reaction mixture. In most cases, isolation of the unreacted amine was difficult unless the reaction time was short, typically below 48 h. On the other hand, residual $[IrCp^*Cl_2]_2$ could be almost quantifiably recovered majority of the time.

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