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Iridium Complexes of the Doubly Cyclometalated NHC Ligand IMes″

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Supporting Information

ABSTRACT: Two consecutive C—H bond activations at the coordination sphere of Ir transform the commonly employed NHC ligand IMes into the new κ^3-C fac-coordinating ligand IMes″. The preparation and structure of Ir(III) complexes featuring this ligand together with selected reactions toward small molecules that illustrate their reactivity keys are described.

N-Heterocyclic carbene (NHC) ligands have found widespread application in transition-metal catalysis and organometallic chemistry,[1] as they offer an extraordinarily wide range of stereoelectronic possibilities.[2] These may be further increased by combining NHCs with themselves or other donor moieties to form bi- or multidentate ligands.[3] For certain metals and oxidation states, bidentate NHC ligands can be generated via C—H bond activations at the N-bound wingtips.[4,5] Just as for cyclometalated phosphines,[6] such bond activations are often reversible,[7] so metalation can be regarded as an additional reactivity resource provided by the ligand.[8] This work shows that one of the most commonly employed NHC ligands, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), is susceptible to double cyclometalation at the coordination sphere of iridium to form the κ^3-C fac-coordinating ligand IMes″. In addition to this stabilizing coordination mode, the new ligand offers strong trans-labilizing capabilities and can be demetalated in a stepwise fashion or functionalized using a variety of reagents.

We recently reported that treatment of the iridium tris(acetonitrile) dihydride $[IrH_2(NCMe)_3(IMes)]PF_6$ with hydrogen acceptors such as ethylene or propylene produces the Ir(III) alkyl derivatives $[Ir(IMes')(R)(NCMe)_2]PF_6$ (R = ethyl or *n*-propyl, respectively), most likely after a sequence of hydrogenation, C—H oxidative addition, and alkene insertion reactions.[9] We have now observed that the slightly more reactive precursor $[IrH_2(\eta^6\text{-}C_6H_6)(IMes)]PF_6$ can drive activation of the NHC ligand beyond the first metalation step, affording Ir(IMes″) complexes. The optimal experimental conditions for this process were found to be warming of propylene-saturated acetone solutions of the precursor arene complex at 328 K for several hours within a closed flask. Even though we have not been able to characterize the intricate mixture of complexes in equilibrium that results from such a treatment, the Ir(IMes″) fragment can be "extracted" from these reacting solutions in good yield in the form of various isolable complexes, as illustrated in Scheme 1. This scheme features cationic, zwitterionic, and neutral Ir(IMes″) complexes coordinating exclusively through carbon atoms (**1**, **3**, and **4**, respectively), together with the cationic tris(acetonitrile) complex **2**. The reactivity and synthetic versatility of these complexes decrease as their numbering increases. Thus, the cyclopentadienyl complex **4** can be synthesized from any of **1**—**3**, while **3** can be obtained from the cationic compounds but not vice versa.

The dehydrogenation pathway observed for our Ir(IMes) precursor contrasts with that previously reported for related Ir(IPr) and Ir(ICy) compounds,[5] where the initial C—H bond activation was followed by a hydrogen β-elimination to yield an alkene, an elementary step not possible for IMes.

Comparison of the structures in Figure 1 with those of related Ir(IMes) and Ir(IMes′) derivatives show that the double cyclometalation does not imply significant distortions of the IMes skeleton.[9] The Ir—N bond distances in the cation of **2** (all >2 Å) confirm that the three acetonitrile ligands trans to IMes″ are weakly bonded[9] and also indicate that the structural trans effect of the alkyl arms exceeds that of the carbene. Accordingly, the acetonitrile ligands of **2** coordinated trans to the methylene carbons were found to exchange readily with acetonitrile-d_3 in $CDCl_3$ solution at room temperature, while the ligand trans to the carbene carbon remained unaffected. The activation parameters for the facile acetonitrile dissociations were estimated by ^1H NMR spin saturation transfer and line-width measurements as $\Delta H^\ddagger = 20 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = 7 \pm 3$ cal K^{-1} mol^{-1} (see the Supporting Information). In spite of these kinetic properties and as previously observed in parent Ir(III) octahedral complexes,[9,10] substitution reactions of **2** with monodentate ligands other than acetonitrile were found to yield the less encumbered substitution products, namely, those with the incoming ligand in the position trans to the carbene carbon. A representative example of such thermodynamic substitution products, the triisopropylphosphine complex $[Ir(IMes'')(NCMe)_2(P\textit{i}Pr_3)]PF_6$ (**5**), is shown in Scheme 2.

Despite their ability to generate coordination vacancies, none of the complexes **1**—**3** were observed to react with conventional sources of hydrogen atoms to reverse the cyclometalation process. Neither dihydrogen at a pressure of 60 bar nor other potential oxidative addition reagents such as triethylsilane, pinacolborane, or phenylacetylene indicated any reaction with the Ir(IMes″) fragment under harsh reaction conditions.[11] On the contrary, the phosphine derivative **5** was found to react with all of these reagents (Scheme 2). First of all, this suggests that these reactions might involve intermediates or transition states with iridium in the Ir(V) oxidation state, which would be attainable by the Ir(IMes″) moiety only with the help of an additional very basic ligand such as the phosphine.

The reaction of **5** with either dihydrogen (1 bar) or excess triethylsilane was found to yield the known dihydride complex

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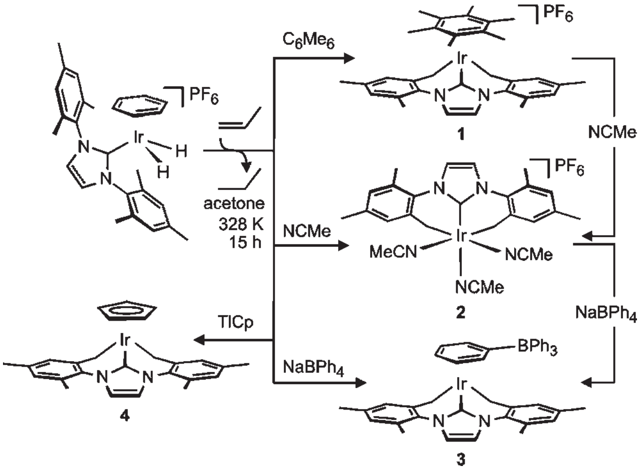
Scheme 1. Synthesis of Ir(IMes′′) Complexes



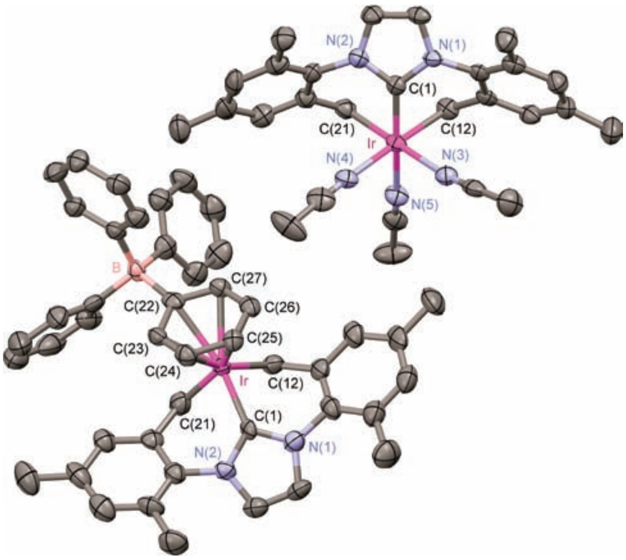
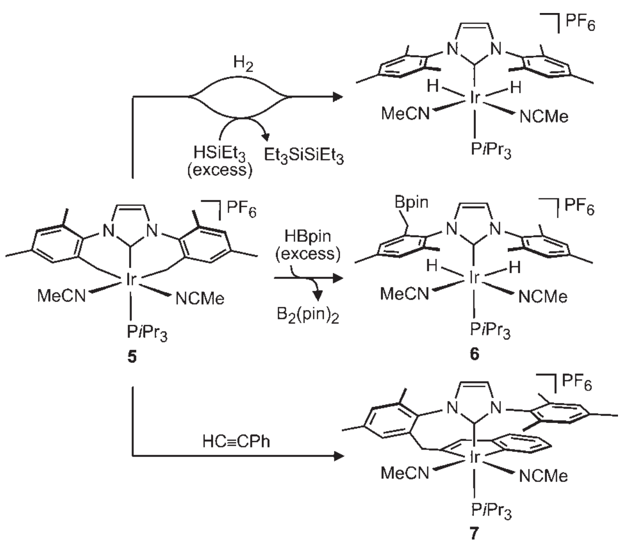


Figure 1. X-ray structures of (top-right) the cation of **2** and (bottom-left) complex **3** (thermal ellipsoids shown at the 80% level). Selected bond distances (Å) and angles (deg) in **2**: Ir−C(1), 1.957(4); Ir−C(12), 2.082(4); Ir−C(21), 2.083(4); Ir−N(3), 2.118(4); Ir−N(4), 2.102(4); Ir−N(5), 2.063(4); C(1)−Ir−C(12), 81.77(17); C(1)−Ir−C(21), 81.69(17). In **3**: Ir−C(1), 1.965(5); Ir−C(12), 2.093(5); Ir−C(21), 2.077(5); Ir−C(22), 2.351(5); Ir−C(23), 2.261(5); Ir−C(24), 2.270(5); Ir−C(25), 2.294(5); Ir−C(26), 2.286(5); Ir−C(27), 2.275(5); C(1)−Ir−C(12), 78.96(19); C(1)−Ir−C(21), 80.1(2).

$[IrH_2(IMes)(NCMe)_2(PiPr_3)]PF_6$.[9] In the case of silane, the reaction consumed 4 equiv of reagent and additionally formed 2 equiv of triethyldisilane. Both reactions were slow at room temperature (days) and involved transient hydride intermediates detectable by NMR spectroscopy.[12] In contrast, the reactions of **5** with pinacolborane and phenylacetylene in excess were observed to be faster (hours) and to lead to complexes with nonsymmetric functionalized IMes ligands after C−B and C−C bond formations, respectively. The different outcomes and rates of these reactions may suggest that IMes′′ functionalization via C−C or C−B bond formation is kinetically favored over the C−Si alternative. Nevertheless, the steric properties of each reagent and the different hybridization at the relevant C, B, or Si atom might also make the difference.

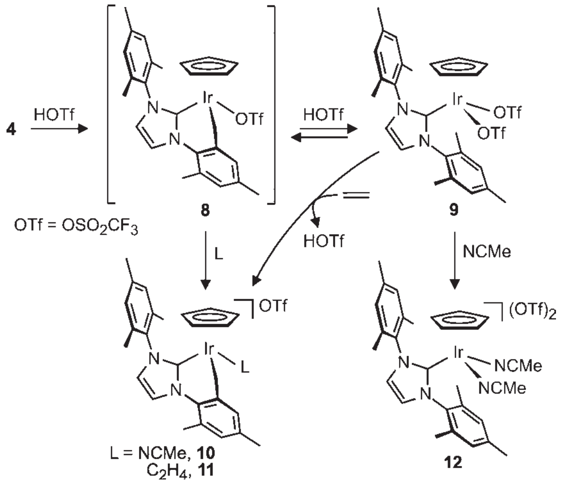
Scheme 2. Selected Reactions of Complex 5 with Small Molecules



As for the silane, the reaction of **5** with pinacolborane consumed excess reagent, cleaving E−H bonds to form E−E ones. With regard to the negative thermodynamic balance of such operations,[13] the likely driving force for the observed reactions is the steric demand of the IMes and $PiPr_3$ ligands,[14] which should favor hydride ligands over the bulkier boryl or silyl ones. The NMR spectroscopic features of the CH_2Bpin moiety in **6** at room temperature (RT) indicated the absence of a symmetry plane, thus revealing restricted bond rotations within the boryl-functionalized IMes ligand. In spite of that, the resonances due to the other ligands were consistent with local C_s symmetry at the metal coordination sphere, although all of these NMR signals displayed a shoulder ($\sim^1/_3$ of the intensity), suggesting that more than one conformational minimum exists for the molecule.

The reaction of **5** with phenylacetylene stresses the capability of these iridium complexes to elaborate organic moieties through C−H bond activation. The characterization of **7** required low temperature (233 K) NMR determinations because the very easy acetonitrile dissociations broaden most of the signals in the RT spectra. The unusual κ^3-C ligand formed after the incorporation of the alkyne into IMes showed three characteristic doublets due to quaternary carbons coupled to phosphorus, which appeared at δ 136.41 ($J_{CP} = 8.9$ Hz), 142.96 ($J_{CP} = 6.5$ Hz), and 150.04 ($J_{CP} = 113.1$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2. The use of the reagent deuterated at the alkyne carbon led to an isotopomer of **7** selectively labeled at the alkenyl CH. This indicates that the C−C bond formation in one wingtip preceded the C−H reductive elimination of the other, suggesting that the C−C bond forms via a vinylidene tautomer of the alkyne. Notably, the reaction between phenylacetylene and an analogue of **5** with a singly cyclometalated IMes, the hydride $[IrH(IMes')(NCMe)_2(PiPr_3)]PF_6$, was reported to begin with a C−H reductive elimination step, yielding a hydride−alkynyl complex as the final product.[9] The comparison illustrates that despite their obvious similarities, the singly and doubly cyclometalated IMes ligands may trigger remarkably different reactivities.

Scheme 3. Protonations of Complex 4



Protonation reactions of the coordinatively saturated neutral derivative **4** (Scheme 3) provided alternative access to a variety of cyclopentadienyl NHC complexes of iridium, which are compounds that have already exhibited very rich chemistry and outstanding catalytic properties.[15]

Treatment of **4** with 2 equiv of triflic acid in chlorinated solvents allowed the synthesis of the neutral bis(triflate) complex **9**. Alternatively, double protonation in the presence of acetonitrile yielded dicationic derivative **12**. The addition of just 1 equiv of the acid to CD_2Cl_2 solutions of **4** was found to give a mixture of products that interconverted rapidly on the NMR time scale at RT. The low-temperature spectra indicated that each of the two major components in this mixture displays a single metalated mesityl group, and these were tentatively assigned as the two likely conformers[9] of the expected product $[Ir(Cp)(IMes')(OSO_2CF_3)]$ (**8**). Although this neutral derivative could not be isolated as an analytically pure solid, its cationic adducts with acetonitrile (**10**) and ethylene (**11**) were prepared by adding the acid in the presence of the desired ligand. Complex **10** consisted of two conformers (~4:3 relative proportion) that readily dissociated acetonitrile and interconverted, while **11** was obtained as a single conformer featuring an anti orientation between the methylene hydrogens and a slow-rotating ethylene ligand. Interestingly, our attempts to prepare an analogue of dication **12** with ethylene ligands instead of acetonitriles systematically afforded **11**, even when we started from previously isolated complex **9** and used excess acid. This indicates that the mono- and bisprotonated species were indeed in equilibrium and suggests that not every ligand is capable of stabilizing the very electrophilic dicationic analogues of **12**.

In summary, we have shown that C−H activation at both mesityl wingtips of the IMes ligand generates a tridentate bis(alkyl) NHC ligand that fits well into fac-coordination positions. This new ligand can contribute very significantly to the reactivity of its compounds by opening vacant coordination sites and forming new bonds in reactions toward protons, dihydrogen, silanes, boranes, or terminal alkynes, all of which are reagents implicated in major catalytic applications of the iridium complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis and characterization details, figures and tables on the kinetic determination, crystal data, and a CIF file for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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