N-Heterocyclic Carbenes

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Double C–H Bond Activation of $C(sp^3)H_2$ Groups for the Preparation of Complexes with Back-to-Back Bisimidazolinylidenes**

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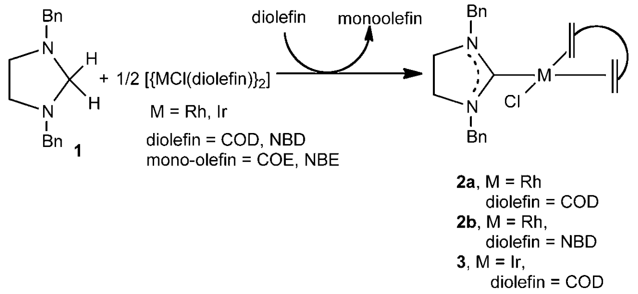
It is now very well recognized that N-heterocyclic carbenes (NHCs) have found an important place in the fields of organometallic chemistry and homogeneous catalysis. Despite their increasing popularity, the coordination of NHCs to transition-metal complexes is limited to a small number of procedures, most of which require the use of azolium salts as carbene precursors.[1] Therefore, the design of new NHCs with novel topologies and improved chemical properties is basically restricted to the availability of their related azolium precursors. In the last few years, several attempts to obtain NHCs from nontraditional precursors have been reported. For example, Hahn and co-workers reported an elegant procedure in which the NHC ligand is generated through a template-controlled cyclization of β-functionalized isocyanides. This approach provides ready access to NH,NH-substituted "protic" NHC ligands.[2]

Because we are interested obtaining NHC-based complexes with new topologies and improved catalytic activities, we are very interested in finding alternative routes to NHC complexes to widen the library of ligand precursors used, so that we can have access to NHC complexes that may not be available from azolium salts. In our search for improved homogeneous catalysts, we prepared a series of homo- and heterodimetallic complexes based on the ligand 1,2,4-trimethyltriazolyldiylidene.[3] The use of heterodimetallic complexes of Ir/Rh and Ir/Pd enabled us to study their activity in catalytic tandem processes in which each metal mediated a mechanistically distinct reaction.[4] Some related dimetallic systems in which the linker between the two metal fragments is a bis(benzimidazolylidene) ligand were also reported by Bielawski and co-workers,[5] although in their case only homometallic complexes were described. The bisylidene ligands described by Bielawski and co-workers and by us have in common their preparation from bisazolium salts that were readily accessed by known literature procedures.[6] Apart from these examples, despite a close review of the literature dealing with N heterocycles, we have not found any further simple bisazolium salts that are suitable precursors to bisylidene linkers between two metal centers. In this regard, we believe that the design of new discrete multitopic carbenes that are poised to bind multiple transition metals may require new strategies for NHC generation.

In certain cases, carbenes can be generated by double C–H bond activation of $C(sp^3)H_2$ groups.[7–9] Although most of the known examples involve the transformation of cyclic ethers into traditional Fischer carbenes,[8] there is one example in which the double $C(sp^3)$ dehydrogenation of a cyclic $H_2C(NRCH_2)_2$ species afforded an Ru–NHC complex.[9] To check the general applicability of this alternative synthetic route to carbene complexes, we investigated the possibility that the N heterocycle **1** (Scheme 1) might react with iridium or rhodium complexes if a hydrogen acceptor was added to the reaction medium to facilitate the formation of the N-heterocyclic carbene.



Scheme 1. Reaction of **1** with rhodium–diolefin and iridium–diolefin complexes in CH_3CN at reflux to give carbene complexes **2** and **3** with formation of the corresponding monoolefin. Bn = benzyl, NBE = norbornene.

To our surprise, the reaction of **1** (R = Bn) with $[\{MCl(cod)\}_2]$ (M = Rh and Ir) in CH_3CN at reflux afforded **2a** and **3** in moderate yields (38% for **2a**, 45% for **3**) without the need to add a hydrogen acceptor. GC analysis of the reaction products revealed that cyclooctene (COE) was formed, and that the amount of the monoolefin corresponded to the yields observed for **2a** and **3**. This result clearly suggests that 1,5-cyclooctadiene (COD) acted as an internal hydrogen acceptor and was released from the metal as COE. Cyclooctane was not detected among the reaction products, so COD is only capable of accepting one molecule of H_2. For stoichiometric reasons, the reaction yield is restricted to a maximum of 50%, unless an external hydrogen acceptor is added to the reaction medium. We performed several experiments in which we

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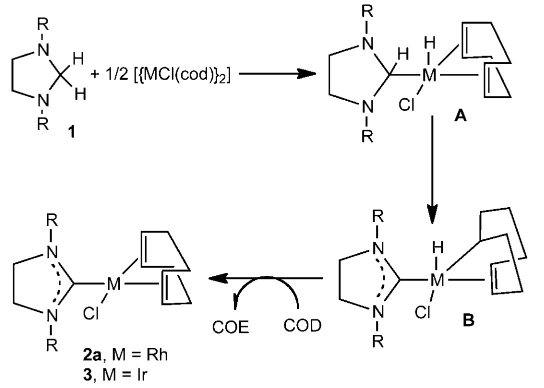
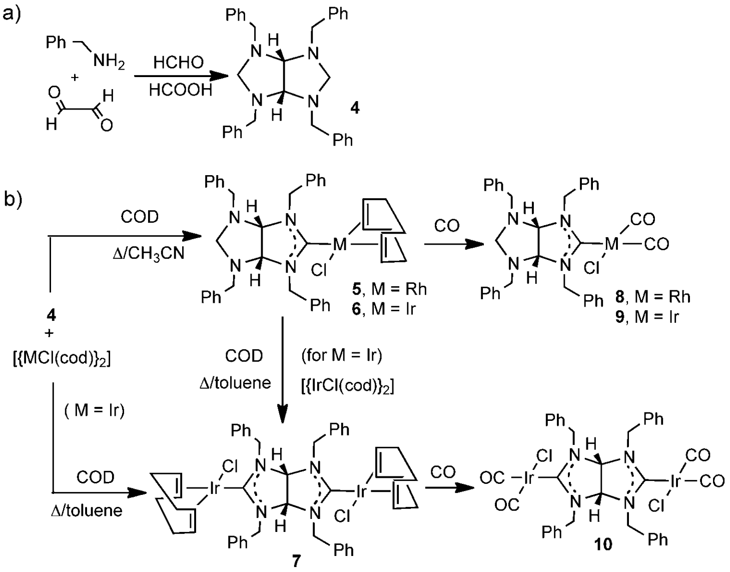
added different classical hydrogen acceptors, such as *tert*-butylethene, acetone, or cyclohexanone, but we did not improve the yields of **2a** and **3**. We also did not observe the formation of the corresponding hydrogenated partners of the hydrogen acceptors used. However, when we added an extra amount of COD (5 equiv), the reaction products were obtained in yields higher than 50% (60% for **2a** and 65% for **3**), which implies that the chelating nature of the hydrogen acceptor is needed to facilitate the process. Again, the formation of COE matched perfectly with the yields of the complexes. To confirm that chelating olefins are needed to promote the process, we carried out a reaction with [{RhCl(nbd)}$_2$] as the metal source and also added 2,5-norbornadiene (NBD; 5 equiv) to the reaction mixture. Under the same reaction conditions as those described above, we obtained the nbd-based complex **2b** in high yield (67%). In contrast, when the reaction was performed with [{MCl(coe)$_2$}$_2$] (M = Rh, Ir), in the presence of excess COE, metalation of the diamino heterocycle did not take place.

Although we did not perform a detailed mechanistic study, we believe that the formation of **2a** and **3** from the reaction of **1** and [{MCl(cod)}$_2$] (M = Rh and Ir) implies the steps depicted in Scheme 2. First, the oxidative addition of a C(sp^3)–H bond to the metal should afford an M^{III} hydride **A**, which may evolve to intermediate **B** through olefin insertion into the M–H bond and α elimination of the N heterocycle. The final step would involve the release of the monoolefin by reductive elimination and the coordination of COD to form the final product (**2a** or **3**). Although we do not have experimental proof of the formation of the intermediates **A** and **B**, we believe that their formation is strongly supported by previously reported results. For example, Shaw and co-workers reported the formation of a pincer-carbene (PCP) iridium complex by C–H oxidative addition and subsequent α elimination with the release of dihydrogen.[10] In the same context, Crabtree and co-workers performed a detailed mechanistic study in which they showed that the formation of an iridium(III) carbene from a 2-dimethylaminopyridine ligand proceeded through a reversible α elimination, which in their case proved to be extremely facile.[11] The oxidative addition of neutral diamino heterocycles is also a known process, as recently described by Hahn and co-workers.[12]

We believed that the unprecedented reaction shown in Scheme 1 should have some important implications for the formation of new NHC complexes that are not accessible from the classical azolium carbene precursors. In this regard, the tetraazabicyclooctane **4**,[13] can be obtained in high yield by the reaction shown in Scheme 3a. The reaction of **4** with [{MCl(cod)}$_2$] (M = Rh and Ir) in acetonitrile at reflux afforded the corresponding mono-NHC species **5** and **6**, although in very low yields (< 30%). When the same reaction was performed in the presence of COD, the products were obtained in much higher yields (55% for **6** and 65% for **5**) with the concomitant production of the same amount of COE. When the reaction with [{IrCl(cod)}$_2$] was carried out in toluene at reflux, the bimetallic compound **7** with a bis-NHC bridging ligand was obtained. Compound **7** can also be obtained from **6** (Scheme 3b).



Scheme 2. Expected steps involved in the formation of **2a** and **3** from **1** and [{MCl(cod)}$_2$].



Scheme 3. Synthesis of the tetraazabicyclooctane **4** and its conversion into mono- and biscarbene complexes.

All compounds **5**–**7** were characterized by means of NMR spectroscopy and mass spectrometry (see the Supporting Information for full details). The ^{1}H NMR spectra of **5** and **6** revealed that the ligand is coordinated to only one metal fragment, as shown by the two doublets due to the inequivalent NCH$_2$N protons of the uncoordinated ring. The ^{13}C NMR spectra confirmed that metalation had occurred, with signals at $\delta = 214$ (doublet, $^1J_{\mathrm{Rh,C}} = 47$ Hz; **5**) and 207.7 ppm (**6**) assigned to the M–C$_{\mathrm{carbene}}$ carbon atom. The ^{1}H NMR spectrum of **7** confirmed the twofold symmetry of the compound. The signals due to the two NCH$_2$N protons disappeared, which indicates that double metalation had occurred. In the ^{13}C NMR spectrum, the signal due to the two equivalent Ir–C$_{\mathrm{carbene}}$ carbon atoms appeared at $\delta =$ 211.2 ppm.

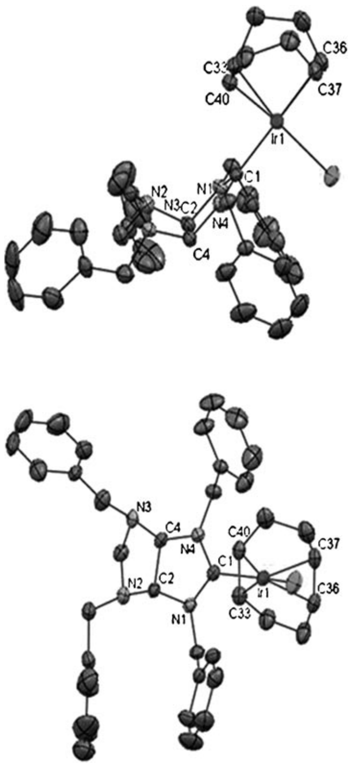


Figure 1. Two perspectives of the molecular structure of **6** (ellipsoids at 30% probability). All hydrogen atoms have been omitted for clarity. Selected distances [Å] and angles [°]: Ir1–C1 2.021(5), Ir1–Cl1 2.3541(17), Ir1–C40 2.093(6), Ir1–C33 2.096(6), Ir1–C36 2.192(6), Ir1–C37 2.195(6); C1-Ir1-Cl1 90.31(16).

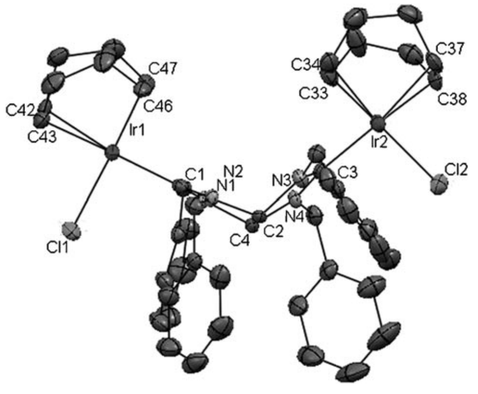
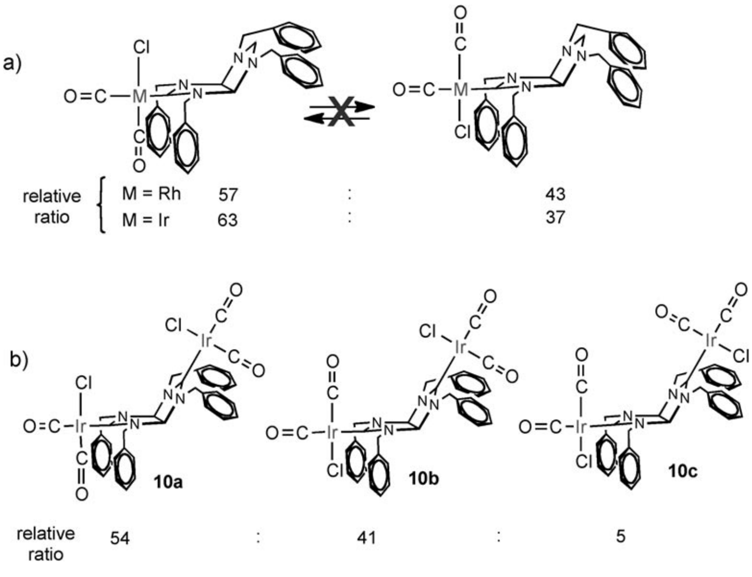


Figure 2. Molecular structure of **7** (ellipsoids at 30% probability). All hydrogen and solvent (hexane) atoms have been omitted for clarity. Selected distances [Å] and angles [°]: Ir1–C1 2.017(7), Ir1–Cl1 2.3509(19), Ir1–C46 2.107(7), Ir1–C47 2.114(8), Ir1–C42 2.202(7), Ir1–C43 2.211(7), Ir2–C3 2.018(7), Ir2–Cl2 2.345(2), Ir2–C34 2.078(9), Ir2–C33 2.087(9), Ir2–C38 2.202(7), Ir2–C37 2.204(7); C1-Ir1-Cl1 90.86(18), C3-Ir2-Cl2 92.47(19).

The molecular structures of **6** and **7** were confirmed by means of X-ray diffraction studies. The structure of compound **6** (Figure 1)[14] confirms the coordination of the bicyclic N-heterocyclic carbene to the Ir^{I} center. One chloride and one cod ligand complete the coordination sphere about the metal center. The Ir–C$_{carbene}$ distance is 2.021 Å. Because the bicyclic ligand is folded along the connecting C(2)–C(4) bond, the four *N*-benzyl groups occupy the less sterically strained orientation, on the outside of the folded structure. The two benzyl groups at the metalated ring are closer to the chloride ligand and thus avoid the bulkier cod ligand.

The molecular structure of **7** (Figure 2) confirms the bimetallic nature of the compound. The molecule has pseudo-C_{2v} symmetry. The bicyclic bis-NHC bridges two iridium fragments, which each complete their coordination sphere with a chloride and a cod ligand. The Ir–C$_{carbene}$ distances are approximately 2.02 Å. Owing to the angular nature of the bicyclic ligand, the through-space distance between the two metal centers is 7.166 Å, whereas the through-ligand distance is 8.5 Å. As observed for the monometallic complex **6**, the *N*-benzyl groups point toward the chloride ligands. The heterocyclic biscarbene ligand displays an average angle of 96.5° with respect to the metal coordination planes.

Compounds **5**, **6**, and **7** were transformed into the corresponding carbonylated complexes by treatment with CO in dichloromethane (Scheme 3). Each carbonylation yielded two rotamers that we could not separate and that we attributed to the restricted rotation of the carbene about the M–C$_{carbene}$ bond. The most stable situation arises from the orientation of the two benzyl groups close to one of the smaller CO ligands; two different rotamers are expected for complexes **8** and **9** (Scheme 4a). Variable-temperature NMR spectroscopic experiments (in [D$_8$]toluene between 25 and 80 °C) together with spin-polarization-transfer (SPT) NMR spectroscopic experiments enabled us to confirm that these two rotamers do not interconvert. In the case of complex **10**, three different rotamers are expected (Scheme 4b). All three



Scheme 4. Rotamers observed for a) the monocarbene complexes **8** (M = Rh) and **9** (M = Ir), and b) the biscarbene complex **10**.

were detected in the corresponding ^{1}H NMR spectrum. Interestingly, this situation does not apply for the cod-substituted complexes **5**, **6**, and **7**, for which the complexes with the benzyl groups close to the chloride ligand are strongly preferred (see the molecular diagrams in Figures 1 and 2) over the related orientation of the benzyl groups close to the bulkier cod ligand. This situation arises from the restricted rotation of the benzyl groups about the N−C bonds owing to the special topology of the ligand. The four benzyl groups are forced to point away from the inner cavity formed by the two planes of the central bicyclic heterocycle. For the monoazole-derived complexes **2** and **3**, the situation is completely different because the benzyl groups are free to rotate about the N−C bonds. Thus, the benzyl groups can adopt the two possible orientations by free N−C rotation, whereas M−C rotation is still restricted.

The existence of the different isomers does not change the local symmetry about the metal centers nor the electron-donating power of the ligands. For this reason, the IR spectra of **8**, **9**, and **10** display only two CO stretching bands, as expected for the *cis* orientation of the carbonyl ligands. For the monometallic compounds, these bands appear at 2077 and 1995 cm^{-1} for **8** and 2063 and 1978 cm^{-1} for **9** and correlate well with those of analogous previously described saturated mono-NHC complexes of Rh[15] and Ir.[16] The CO stretching bands of the bimetallic compound **10** appear at 2071 and 1986 cm^{-1} and thus indicate that the double coordination of the biscarbene ligand slightly lowers the electron-donating capacity of the carbene with respect to that of its mono-coordinated form.

In conclusion, we have shown that saturated N-heterocyclic carbenes of rhodium and iridium can be readily prepared by the simple treatment of cyclic neutral N heterocycles with widely used $[\{\mathrm{MCl(diolefin)}\}_2]$ metal sources. The reactions can be triggered by the addition of an external amount of 1,5-cyclooctadiene or 2,5-norbornadiene, which act as hydrogen acceptors, and offer several advantages over the use of regular preligand-activating agents when azolium salts are used. This method to generate NHC complexes enables the ready preparation of new metal compounds with sophisticated architectures, as demonstrated with complexes **5**–**10**. The possibility of preparing dimetallic complexes suggests that we may soon find a way to prepare heterodimetallic species, potentially useful for the design of new tandem catalytic processes. Studies to extend the use of our new biscarbene ligand to other metal species and explore the catalytic properties of the resulting complexes are underway.

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[14] CCDC 816602 (**6**) and 816603 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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