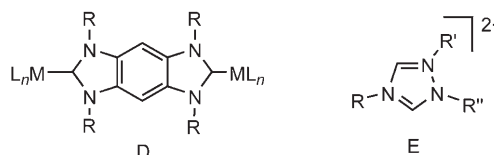


Triazolediylidenes: A Versatile Class of Ligands for the Preparation of Discrete Molecules of Homo- and Hetero-Binuclear Complexes for Improved Catalytic Applications**

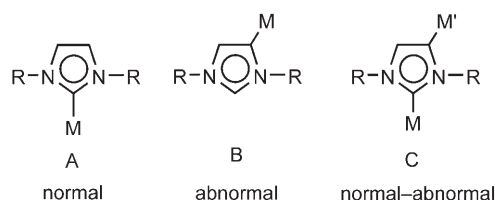
Elena Mas-Marzá, José A. Mata, and Eduardo Peris*

It is well-recognized that N-heterocyclic carbenes (NHCs) have appeared as a versatile class of ligands in the preparation of new homogeneous catalysts.^[1] Their chemical versatility not only implies a wide variety of structural diversity and coordination modes, but also their capability to form stable complexes with a large number of transition metals with different oxidation states augments their versatility. Another interesting feature of NHCs is that they can show two types of coordination, depending on which carbon atom is bound to the metal center, and are thus classified as normal (C2-bound, A in Scheme 1) and abnormal (C4-bound, B in Scheme 1)

type), thus forming homo-binuclear complexes of rhodium, palladium, platinum, and silver (D, Scheme 2).



Scheme 2. Janus-type NHC ligands with facially opposed coordination abilities.



Scheme 1. Coordination modes of NHCs.

carbenes as a consequence of the studies first reported by Crabtree and co-workers.^[2] Under these circumstances, it is not difficult to imagine a situation with simultaneous coordination of two metal fragments at the C2 and C4 positions of the azole ring, resulting in a new ditopic form of coordination of the NHC (C, Scheme 1). However, the latter situation is still unknown, although a wide scope of applications can be envisaged.

A related situation to that shown in C (Scheme 1) was recently reported by Bielawski and co-workers,^[3] who described a series of benzobis(imidazolyliene)s. These compounds show facially opposed coordination abilities (Janus-

Triazolilydenes are a class of NHCs that has not been as widely explored as imidazole-based carbenes. The possibility of obtaining dicationic triazolium biscarbene precursors^[4] (E, Scheme 2) to potentially bind two metal centers was suggested early on by Bertrand and co-workers,^[5,6] who described a polymeric silver biscarbene compound.^[6] Despite the obvious interest in the design of new molecular architectures, discrete molecules with this type of ligand have not yet been reported.

We describe herein the coordination of 1,2,4-trimethyl-triazole-3,5-diylidene, which affords discrete homo- and hetero-binuclear complexes of rhodium and iridium. We also report the exploratory screening of the catalytic activity of one of the Ir complexes in transfer hydrogenation and intramolecular cyclization of alkynoic acids.

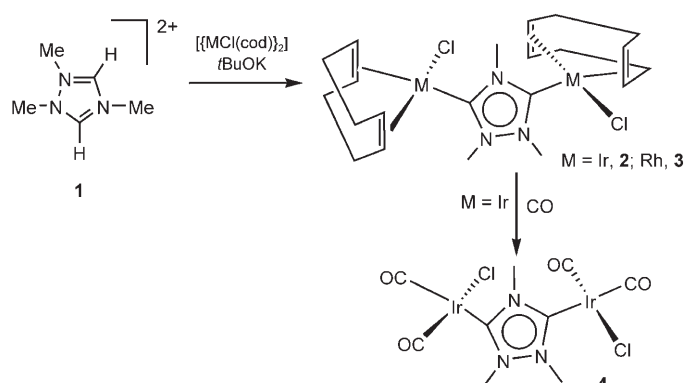
The trimethyltriazolium dication **1** reacted with $[\{MCl(cod)\}_2]$ ($M = Ir, Rh$; $cod = 1,5$ -cyclooctadiene) in the presence of *t*BuOK in THF heated at reflux to afford the dinuclear compounds **2** (Ir) and **3** (Rh), as shown in Scheme 3. The NMR spectroscopic data of **2** and **3** revealed that metalation of the biscarbene had occurred, as evidenced by the presence of signals at $\delta = 187.5$ (**2**) and 191.4 ppm (**3**, $^1J(Rh, C) = 43$ Hz) in the ^{13}C NMR spectra, assigned to two equivalent metalated carbon atoms. Compound **2** readily reacts with CO to yield the tetracarbonyl complex **4**. The 1H NMR spectrum of **4** only shows two signals in a 2:1 ratio, which are due to the *N*-methyl groups of the azole ring. The signal corresponding to the carbene carbon atom appears at $\delta = 181.9$ ppm in the ^{13}C NMR spectrum.

The molecular structures of **2** and **4** were confirmed by means of single-crystal X-ray diffraction. The structure of **2** (Figure 1) consists of a dinuclear molecule with two Ir centers in a pseudo-square-planar configuration. The bridging azole ring is coordinated to the metal centers through the carbon atoms, with a Ir–C_{carbene} bond length of 2.006 Å, which is in the

[*] E. Mas-Marzá, J. A. Mata, E. Peris
Departamento de Química Inorgánica y Orgánica
Universitat Jaume I
12071 Castellón (Spain)
Fax: (+34) 964-728214
E-mail: eperis@qio.uji.es

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Supporting information for this article (including experimental details) is available on the WWW under <http://www.angewandte.org> or from the author.



Scheme 3. Synthesis of complexes **2–4**. The counterion of compound **1** is BF_4^- .

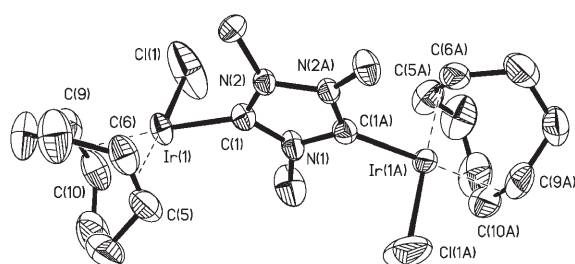


Figure 1. ORTEP view of **2**, ellipsoids set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.006(7), Ir(1)–C(6) 2.092(8), Ir(1)–C(5) 2.118(9), Ir(1)–C(10) 2.197(8), Ir(1)–C(9) 2.209(8), Ir(1)–Cl(1) 2.337(3); C(1)–Ir(1)–Cl(1) 88.4(2).^[16]

range of other Ir triazolylienes described recently.^[7] The two Ir atoms are in the plane of the azole ring, with the chlorine ligands arranged perpendicular to this plane in a relative *anti* disposition. The Ir–C bonds to the olefin *trans* to the carbene are slightly longer than those to the other olefin because of the *trans* influence of the NHC ligand.

The ORTEP diagram of **4** is shown in Figure 2. The structure consists of a dinuclear Ir compound with a bridging triazolediylidene ligand. Two carbonyl groups and a chlorine ligand complete the pseudo-square-planar arrangement around each metal atom. The Ir–C_{carbene} bond lengths are 2.062 and 2.073 Å.

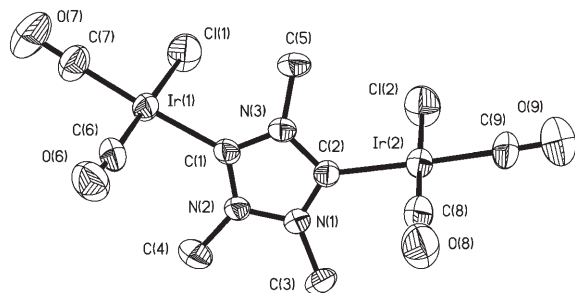
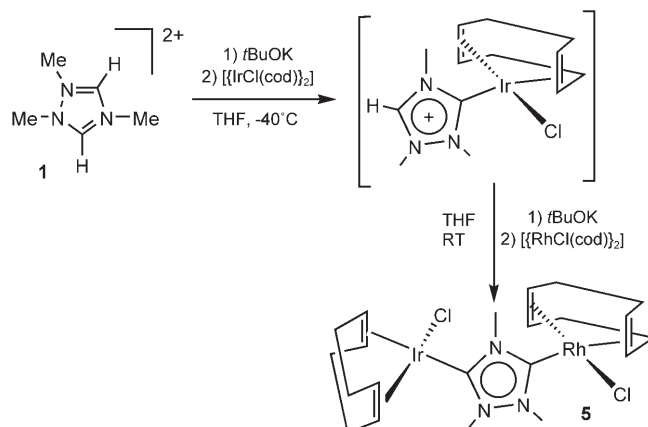


Figure 2. ORTEP view of **4**, ellipsoids set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.062(8), Ir(1)–C(6) 1.843(10), Ir(1)–C(7) 1.865(11), Ir(1)–Cl(1) 2.355(3), Ir(2)–C(2) 2.073(9), Ir(2)–C(8) 1.847(11), Ir(2)–C(9) 1.974(11), Ir(2)–Cl(2) 2.345(3); C(1)–Ir(1)–Cl(1) 88.8(2), C(1)–Ir(1)–C(6) 90.5(4), C(2)–Ir(2)–Cl(2) 89.8(2), C(2)–Ir(2)–C(8) 91.2(4).^[16]

The infrared spectrum of **4** provided interesting information about the electron-donating ability of the biscarbene ligand by allowing the determination of the Tolman electronic parameter (TEP).^[8] The spectrum shows two CO stretching bands (2072, 1987 cm^{-1}), consistent with the *cis* arrangement of the carbonyl ligands. Extrapolating from the known data for metal phosphine complexes, and also recently for metal NHC complexes,^[9,10] the equation^[9] $\text{TEP} = 0.722 \times \nu_{\text{av}}(\text{CO}) + 593 \text{ cm}^{-1}$ gives an estimated TEP of 2059 cm^{-1} . This value is higher than for other known carbenes (2048–2051 cm^{-1})^[10] and even higher than for trialkylphosphines such as PCy_3 (2056 cm^{-1}). In fact, this finding indicates that the triazolediylidene ligand is electronically similar to phosphines, with lower electron-donating ability power than other known NHCs.

In an attempt to check if we could easily obtain hetero-binuclear species from **1**, we decided to perform the deprotonation of the triazolium salt in two steps, with addition of $[\text{IrCl}(\text{cod})]_2$ after the first deprotonation and $[\text{RhCl}(\text{cod})]_2$ after the second. In order to minimize the formation of **2**, we performed the first deprotonation and addition of the Ir precursor at -40°C and subsequently carried out a second addition of base and the Rh precursor at room temperature (Scheme 4). The reaction probably pro-



Scheme 4. Synthesis of complex **5**. The counterion of cationic compounds is BF_4^- .

ceeds through an iridium monometalated cationic species, as shown in Scheme 4. This process allowed us to obtain the Rh–Ir complex **5** in moderate yield, thus confirming the capability of the ligand to easily coordinate to two different metals.

The ^1H NMR spectrum of **5** displays a complicated set of signals arising from the unsymmetric cod ligands. The protons of the three *N*-methyl groups appear as three signals, suggesting the unsymmetric coordination of the triazolediylidene ligand. The ^{13}C NMR spectrum shows signals resulting from the Rh-bound C_{carbene} ($\delta = 191.4 \text{ ppm}$, $^1J(\text{Rh}, \text{C}) = 43 \text{ Hz}$) and the Ir-bound C_{carbene} atoms ($\delta = 187.4 \text{ ppm}$), thus confirming that dimetalation has occurred.

In a preliminary exploratory study of the catalytic activity of these new complexes, we used diiridium complex **2** in transfer hydrogenation and intramolecular cyclization of

alkynoic acids. The Rh complex **3** was also tested in the latter reaction. Complex **2** turns out to be an excellent catalyst in the reduction of ketones and imines. The reactions were carried out in *i*PrOH, using KOH as base. Conversions of aliphatic ketones were complete in 30 min, while *N*-benzylideneaniline and aromatic ketones were completely reduced in 1 h under the reaction conditions used (see the Supporting Information). This result confirms that **2** is a very active species in this type of reaction. Its catalyst efficiency is close to that recently reported by Crabtree and co-workers for monodentate triazole-derived NHC complexes of Ir^[11] and better than the imidazole NHC Ir compounds reported by Nolan and co-workers.^[12]

Probably more relevant is the catalytic activity in the intramolecular cyclization of acetylenic carboxylic acids. Compounds **2** and **3** show full conversion of 4-pentynoic acid in 3 and 8 h, respectively, under the reaction conditions used (see the Supporting Information). The more inert 5-hexynoic acid is fully converted into the corresponding cyclic compound in 7 or 8 days (see the Supporting Information), when **2** or **3** was used, respectively. These results are clearly better than our previously reported results on this type of reaction,^[13,14] where trinuclear complexes of Rh and Ir were also used.^[13] Remarkably, **2** is the first Ir complex to be highly active in this type of reaction, since other Ir catalysts are clearly less efficient than their Rh analogues.^[15]

In summary, we have reported the coordination of a triazolediylidene ligand to Rh and Ir and have fully characterized the resulting complexes. The electron-donating ability of the ligand has been determined in terms of the TEP parameter, from which it was found to be as strongly electron-donating as alkylphosphines. The connection of two catalytically active metal fragments through an aromatic linker may also have interesting implications for their catalytic cooperativity. The preparation of these new molecules allows novel strategies for the design of new homo- and hetero-binuclear species with potentially improved catalytic properties. In fact, the effective preparation of the Ir–Rh species **5** opens the possibility for an extremely wide range of bimetallic combinations, especially if we take into account the high coordination versatility of NHCs. This property makes the triazolediylidene ligand a unique building block for the preparation of tandem catalysts, an effort that is currently underway.

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