# A planar chelating bitriazole N-heterocyclic carbene ligand and its rhodium(III) and dirhodium(II) complexes†

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**The new ligand bitriazole-2-ylidene (bitz) reliably chelates to Rh under very mild conditions, providing an NHC analogue of 2,2′-dipyridyl ligand.**

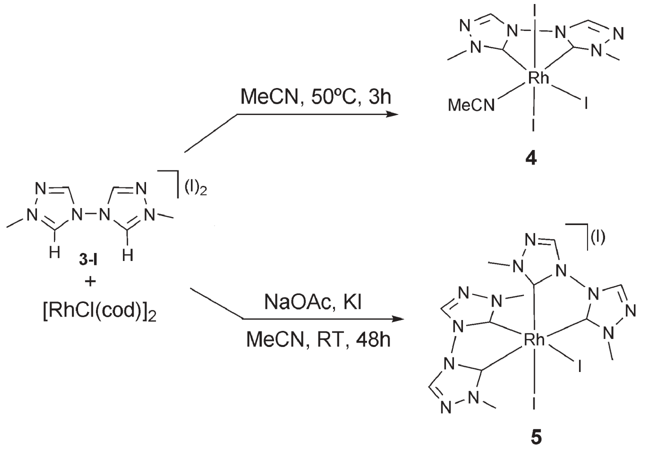
N-heterocyclic carbenes (NHCs) form a sterically and electronically tunable set of ligands that have proved extremely useful in catalysis.[1–5] The ubiquitous imidazol-2-ylidines tend to have a much higher donor power[6–8] than the familiar phosphine ligand set and thus attention has recently begun to turn to the 1,2,4-triazol-2-ylidene NHCs which have a donor power closer to that of $PR_3$.[9]

Chelate-*N*-heterocyclic ligands allow more delicate tuning of topological properties such as steric hindrance, bite angle, chirality and fluxional behavior.[2,10] Unfortunately, the linkers typically used, $(CH_2)_n$ ($n$ = 1–4), may promote the formation of undesired non-chelating species such as **1** (Chart 1), and may also give Hoffmann elimination when strong nucleophiles are used such as in the deprotonation of the biazolium ligand precursors.

In the work reported here, we show the wide versatility of the bitriazol-2-ylidene ligand, **2**, (bitz) which has a planar structure thanks to a direct N–N bond linking the azole rings. The ligand, which might be considered the NHC analogue of the very useful N-donor ligand 2,2′-dipyridyl, is rapidly assembled thanks to the availability of parent bitriazole and its 1,1′-dimethyl derivative, **3**.[11]

We now find that the precursor **3** reliably chelates on metallation under the conditions shown (Scheme 1) providing a series of bitz-based complexes including a surprising di-Rh(II) species.

The usual Rh(I) precursor $[RhCl(cod)]_2$ readily reacts with the iodide salt of **3** and KI, in MeCN at 50 °C over 3 h, to give a Rh(III) product, **4** (Scheme 1). Remarkably, in contrast with previous cases, the addition of an external base is not needed to promote the metallation. A chelate complex is formed, with one acetonitrile and three iodo ligands completing the coordination sphere about Rh(III). The reaction goes under milder conditions than previously found for typical NHCs,[12,13] suggesting that bitz metallates more easily, probably because the higher acidity of the bitriazolium precursor facilitates the activation of the C2–H bonds. The structure of **4** was determined by X-ray diffraction, the details of which are given in the ESI.‡ The molecular structure is also consistent with the spectroscopic data. In particular, the $^{13}C$ NMR spectrum shows two doublets for the distinct carbene carbons at $\delta$ 166.5 ($J_{Rh–C}$ = 42.4 Hz) and $\delta$ 158.2 ppm ($J_{Rh–C}$ = 43.8 Hz).



Scheme 1

Addition of the mild base NaOAc to the reaction mixture used in the synthesis of **4**, leads to the formation of diiodide **5**, a complex having two chelating bitz ligands (Scheme 1). The bis-chelate is still formed even with a 1 : 1 ratio of Rh : bitz, but a 1 : 2 ratio is preferred for synthetic efficiency. The two bitz ligands are mutually *cis*, in contrast to a related bis-chelate bis-NHC reported recently by Youngs and co-workers[14] in which the four NHCs are mutually *trans*, occupying the equatorial coordination sites. As expected for this structure, two inequivalent carbene carbons [$\delta$ 167.1 ($J_{Rh–C}$ = 34.9 Hz) and $\delta$ 162.7 ppm ($J_{Rh–C}$ = 43.6 Hz)] and two peaks due to the N-methyl groups were observed in the $^{13}C$ NMR spectrum of **5**. Other metal complexes bearing chelating poly-carbene ligands have been reported in the literature as, for instance, tripod complexes described by Fehlhammer,[15] Meyer[16] and Smith.[17]

The molecular structure of compound **5** (Fig. 1), determined by X-ray diffraction, is consistent with the spectroscopic data. The $Rh–C_{carbene}$ distances are similar to those reported for other chelating Rh(III) compounds. The bite angles of 78.6(3) and

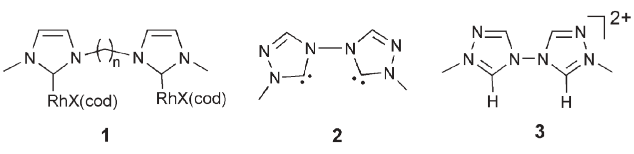


Chart 1

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† Electronic supplementary information (ESI) available: Crystallographic (**4–6**) and experimental (**3–6**) data. See DOI: 10.1039/b705246d

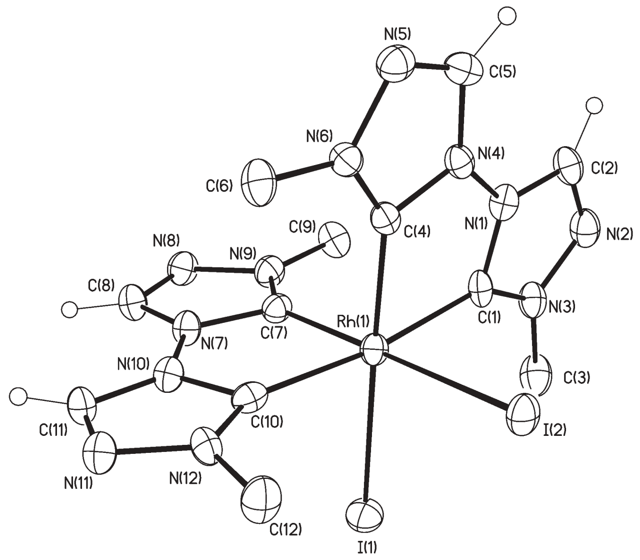


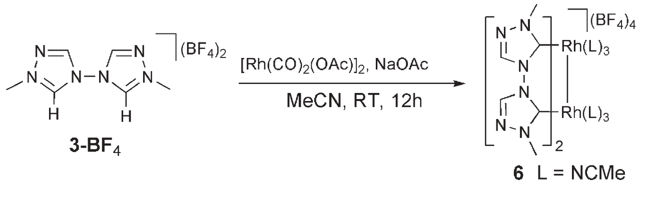
**Fig. 1** Molecular structure of the cation of **5**. Selected bond distances (Å) and angles (°): Rh(1)–C(4) 2.002(6), Rh(1)–C(1) 2.043(6), Rh(1)–C(7) 1.991(6), Rh(1)–C(10) 2.049(7), C(4)–Rh(1)–C(1) 78.6(3), C(7)–Rh(1)–C(10) 79.3(2).‡

79.3(2)° are the smallest so far reported for a chelating bis-NHC ligand. As can be seen in Fig. 1, compound **5** is chiral, although a racemic mixture was obtained.

In an attempt to make the $[\text{bitzRh(CO)}_2]^+$ cation for IR spectroscopy, we performed the reaction of the bitriazolium precursor **3**–$BF_4$ with $[Rh(CO)_2(OAc)]_2$. Contrary to our expectations, the dirhodium(II) complex **6** (Scheme 2) was isolated. Although numerous dirhodium(II) complexes are known, this is the first to contain an NHC ligand.

The structure of **6**, determined by X-ray diffraction (Fig. 2), has a number of unusual features compared with previous dirhodium(II) complexes. This appears to be the first case of a dirhodium(II) complex with a six membered chelate ring. No doubt for this reason, the structure becomes staggered, not eclipsed, the rather rigid bitz ligand being incapable of forming two parallel C–Rh bonds in the planar configuration. This makes the complex chiral. Two singlets due to the N-methyl groups are observed in the NMR spectrum, suggesting that the chiral structure is retained in solution. The length of the Rh–Rh bond (2.65 Å) is within the range reported for other dinuclear Rh(II) compounds with two chelate rings.[18] In all cases the ligands bind *via* the C5 carbon rather than *via* C3.[19] Other structural parameters are unexceptional.

The structure of **6** is also consistent with the spectroscopic data; the $^{13}$C NMR spectrum shows two doublets due to the distinct carbene carbons [$\delta$ 161.7 ($J_{\text{Rh–C}}$ = 51.1 Hz) and $\delta$ 161.1 ppm ($J_{\text{Rh–C}}$ = 53.6 Hz)].



**Scheme 2**

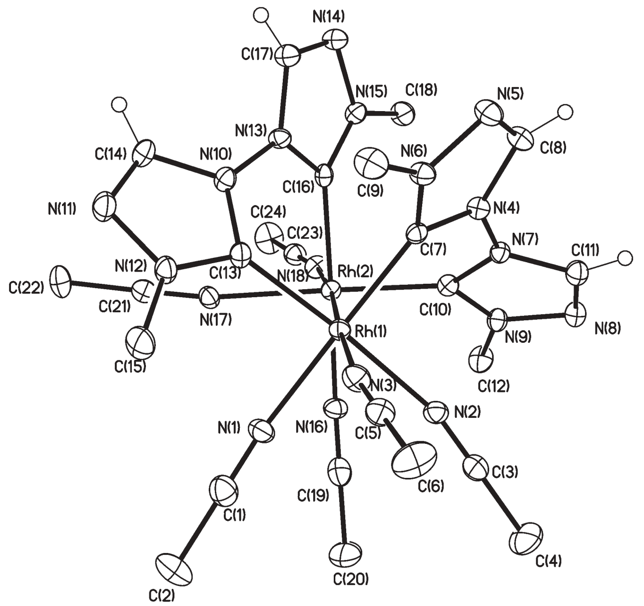


**Fig. 2** Molecular structure of the cation of **6**. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.6459(8), Rh(1)–C(7) 1.969(3), Rh(1)–C(13) 1.979(3), Rh(2)–C(16) 1.972(3), Rh(2)–C(10) 1.993(3), Rh(2)–Rh(1)–C(7) 90.90(9), Rh(2)–Rh(1)–C(13) 87.92(9).‡

Some of these complexes prove to be catalytically active even with the small methyl wingtip groups used here. For example, **4** catalyzes the transfer hydrogenation of acetophenone, cyclohexanone, benzophenone and benzylidene aniline with $^i$PrOH/$^t$BuOK at 82 °C and 1% catalyst loading, giving quantitative yields of the C=O or C=N reduction products after a few hours (see ESI†). The observed yields in the hydrogenation of aromatic ketones are similar to those observed with other chelating Rh(III) complexes bearing bi-imidazole-2-ylidene ligands. Although complex **4** also performed as hydrogen transfer catalyst for aliphatic ketones, the rates were significantly slower compared to the rhodium complexes mentioned above.[12]

The dirhodium complex **6** is also catalytically active in transfer hydrogenation of acetophenone and benzophenone with $^i$PrOH/$^t$BuOK with similar rates to **4**.

In conclusion, the range of compounds formed clearly illustrates the coordinative versatility and high chelating tendency of the bitz ligand and its potential for wide application to transition metal chemistry. The mild reaction conditions for the coordination of the bitz ligand contrasts to those for other related bis-NHC ligands reported so far, thus improving its range of application.

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## Notes and references

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