

# A methylene-bis-triazolium ligand precursor in an unusual rearrangement of norbornadiene to nortricyclyl†

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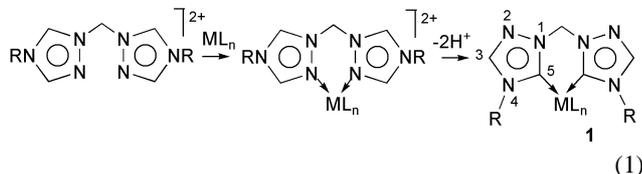
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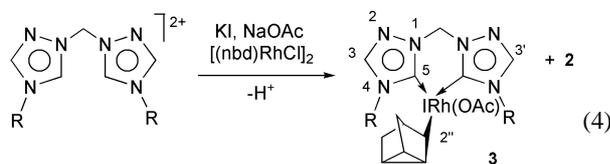
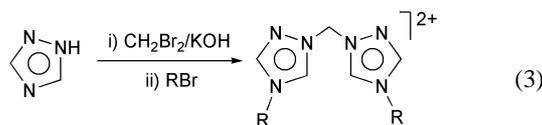
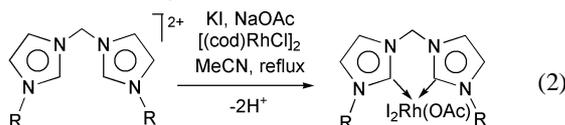
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## Reaction of [(nbd)RhCl]<sub>2</sub> with a chelating bis-[1,2,4]-triazolium salt gives a nortricyclyl Rh complex.

N-Heterocyclic carbenes (NHCs) are of current organometallic interest for their many useful applications in synthesis and catalysis.<sup>1</sup> Most such work involves imidazolium derivatives, but we now report results with 4,4'-dialkyl-bis-[1,2,4]-triazolyl-methane ligand precursors (eqn. 1), where we expected C–H metallation might be facilitated by prior N,N' binding. Mono-dentate triazol-5-ylidene derived ligands are still rare<sup>2</sup> and no chelating examples like **1** are known for rhodium.



In prior work we showed how chelating bis-imidazolium salts ([LH–LH]<sup>2+</sup>) can react with various Rh and Ir precursors to give chelates [(L–L)M]<sub>2</sub>(OAc) (M = Rh or Ir) (eqn. 2) that are highly active for hydrogen transfer catalysis, even in air.<sup>3</sup> We now report the syntheses (eqn. 3, 4) of chelating bis-triazol-5-ylidene derivatives *via* rapid direct metallation of [(nbd)RhCl]<sub>2</sub> (nbd = norbornadiene) to give a Rh(III) species (eqn. 4) with three fac C-bound ligands. A nortricyclyl group derived from the nbd ligand is *cis* to the azole chelate.



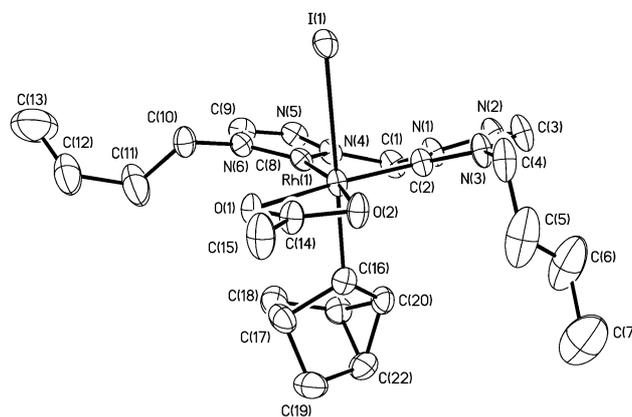
(a, R = n-Bu; b, R = CH<sub>2</sub>Ph)

The precursor salts were readily synthesized by the procedure of eqn. 3. [1,2,4]-triazole alkylates first at the 1 position and then at the 4 position.<sup>4</sup> The syntheses of the Rh complex (eqn. 4) followed the reported procedure of eqn. 2 but the reaction time was shorter (5 h vs. 16 h) showing the higher reactivity of the triazolium over the imidazolium precursor.<sup>5</sup> The pale yellow complex was purified by gradient column chromatography to give *ca.* 45% yield of **3**, fully characterized here.<sup>‡</sup> Some of the

expected bis-iodide complex **2** [(L–L)RhI<sub>2</sub>(OAc)] was also formed.

The puzzling complexity of the <sup>1</sup>H and <sup>13</sup>C NMR spectra for **3** prompted us to do a crystallographic study (see below). This showed a chelating bis-triazolyl-5-ylidene *cis* to a 2-nortricyclyl (ntc) in an overall fac arrangement, so the complexity of the NMR spectrum arises from the loss of the C<sub>2v</sub> symmetry in the bis-triazolyl-5-ylidene ligand and the inequivalence of all ntc protons. Spectral assignments (see ESI†) have been made here by HETCOR and COSY experiments. Compounds **3a** (R = n-Bu) and **3b** (R = CH<sub>2</sub>Ph) show the same patterns in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra in CDCl<sub>3</sub>, except for the alkyl substituents. In particular, for **3a** the <sup>1</sup>H spectrum shows inequivalent H-3 and H-3' protons at 8.05 and 8.04 ppm. The diastereotopic CH<sub>2</sub> bridge protons—accidentally degenerate in CDCl<sub>3</sub>—now form a mutually coupled AB system (d<sup>8</sup>-toluene: 6.03, 5.87; *J* = 12.5 Hz). Proton H-2'' appears as a doublet (δ 2.87 ppm) owing to its coupling with rhodium. (*J*<sub>H–Rh</sub> = 3.2 Hz). The <sup>13</sup>C{<sup>1</sup>H} NMR spectra in CDCl<sub>3</sub> show two doublets at 171.05 and 170.92 ppm (*J*<sub>C–Rh</sub> = 53.8 Hz) corresponding to the two different triazol-5-ylidenes bonded to rhodium and one doublet at δ 52.4 ppm (*J*<sub>C–Rh</sub> = 26.0 Hz) for the ntc alkyl carbon directly bonded to rhodium. The difference in the size of the coupling constant is related to the *s* character of the Rh–C bond: the sp<sup>3</sup> ntc alkyl shows only about half the coupling constant compared to the sp<sup>2</sup> C<sub>carbene</sub>–Rh, because of the higher *s* character in the latter. This correlation extends to other Rh complexes, with *J*<sub>(Rh–C)</sub> following the sequence *J*(azoles, ≈ 50 Hz) > *J*(phenyl, ≈ 40 Hz) > *J*(alkyls, ≈ 25 Hz). High temperature NMR data (d<sup>8</sup>-toluene, 95 °C) show no change occurs.

Crystals of compound **3a** suitable for X-ray diffraction§ were obtained by slow evaporation from Et<sub>2</sub>O. This is only the second example of a crystallographically characterized transition metal-nortricyclyl complex.<sup>6</sup> The Rh (Fig. 1) is octahedral

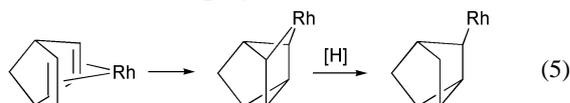


**Fig. 1** Ortep view of **3a** (30% probability level, H atoms omitted). Selected bond lengths (Å) and angles (°). Rh(1)–C(2) 1.955(2), Rh(1)–C(8) 1.949(5), Rh(1)–C(16) 2.081(6), Rh(1)–O(1) 2.164(3), Rh(1)–O(2) 2.159(3), Rh(1)–I(1) 2.8615(11), C(2)–Rh(1)–C(8) 86.7(2), C(2)–Rh(1)–C(16) 93.5(2), C(8)–Rh(1)–C(16) 94.9(2), I(1)–Rh(1)–C(16) 176.94(16), C(2)–Rh(1)–I(1) 83.33(16), O(1)–Rh(1)–O(2) 60.71(12), C(2)–Rh(1)–O(1) 166.19(17), O(2)–Rh(1)–I(1) 89.90(11).

† Electronic supplementary information (ESI) available: <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data for **3a** and **3b**. See <http://www.rsc.org/suppdata/cc/b2/b210726k/>

with the two triazole rings of the chelating ligand (bite angle =  $86.7(2)^\circ$ ) having a dihedral angle of  $26.7^\circ$  with C(1)  $0.65 \text{ \AA}$  below the  $\text{RhC}_2\text{O}_2$  plane. Rh–C distances for NHCs are usually near  $2 \text{ \AA}$ ; here they are slightly shorter ( $1.95 \text{ \AA}$ ) as is usual for chelating bis-NHCs. The high *trans* effect of the carbenes and the alkyl ligand encourages a *fac* geometry and makes the Rh–OAc and Rh–I distances longer than in typical Rh(III) carboxylates (by  $0.15 \text{ \AA}$ ) or in the diiodide **2** (by  $0.20 \text{ \AA}$ ). Compounds **3** are chiral owing to the unsymmetrical ntc ligand. Five of the seven ntc carbons are stereogenic. Nonchelating triazol-5-ylidene rhodium complexes have been prepared.<sup>7</sup>

The mechanism of eqn. 4 has not yet been studied but a plausible pathway (eqn. 5) involves oxidative coupling of nbd to give the corresponding metallacyclobutane intermediate, followed by reductive elimination with an adjacent Rh–H.<sup>8</sup> Mechanistic studies are in progress.



In summary, a new class of bis-chelating NHC is involved in an unusual norbornadiene to nortricyclyl rearrangement.

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## Notes and references

‡ nbd = norbornadiene; ntc = nortricyclyl; cod = 1,5-cyclooctadiene. Synthesis of **3**. A mixture of 1,1'-methylenebis(4-alkyl-1,2,4-triazolium) dibromide (R = benzyl or n-Bu) (0.5 mmol), NaOAc (155.6 mg, 1.9 mmol), KI (315.4 mg, 1.9 mmol) and [(nbd)RhCl]<sub>2</sub> (115.3 mg, 0.25 mmol) was stirred in EtCN (20 ml) at reflux for 5 h. After cooling, the volatiles were removed under reduced pressure and the residue purified by gradient column chromatography. Elution with  $\text{CH}_2\text{Cl}_2$ –acetone (20:1) gave the title

compounds as orange–yellow solids in *ca.* 45% yield. Analytically pure material was obtained from  $\text{CH}_2\text{Cl}_2$ –pentane. Anal. Calc. for compound **3b** ( $M = 712.4$ ). C 47.2, H 4.24, N 11.80. Found C 47.1, H 4.29, N 11.34%. § Crystal data for **3a**: yellow plates ( $0.30 \times 0.20 \times 0.15 \text{ mm}^3$ ),  $M = 644.36$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 8.5969(17)$ ,  $b = 12.062(2)$ ,  $c = 13.182(3) \text{ \AA}$ ,  $\alpha = 84.79(3)$ ,  $\beta = 80.10(3)$ ,  $\gamma = 82.72(3)^\circ$ ,  $V = 1332.3(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.606 \text{ g cm}^{-3}$ ,  $\mu = 18.28 \text{ cm}^{-1}$ , Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), 9133 reflections collected, 6017 unique, observed reflections ( $I > 2.00\sigma(I)$ ) 290 parameters and converged with unweighted and weighted agreement factors of  $R = 0.0408$  and  $R_w = 0.1054$ ,  $S = 0.890$ . CCDC 179138. See <http://www.rsc.org/suppdata/cc/b2/b210726k/> for crystallographic data in CIF or other electronic format and NMR spectral assignments for **3**.

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