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Chelating bis-carbene rhodium(III) complexes in transfer hydrogenation of ketones and imines†

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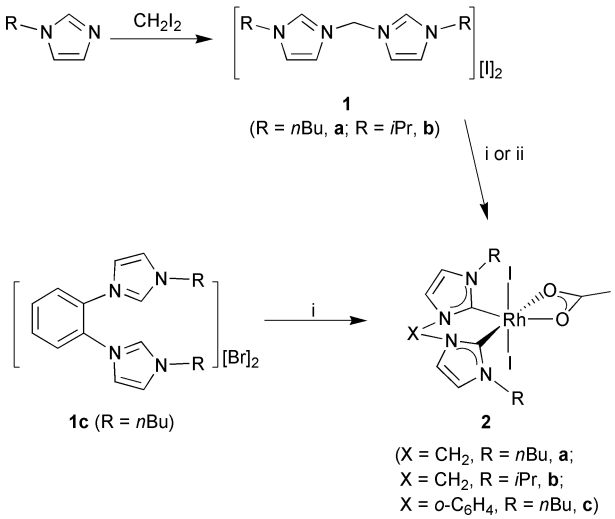
Chelating rhodium(III) carbene complexes are accessible *via* a simple synthesis and are catalytically active for hydrogen transfer from alcohols to ketones and imines.

Homogeneous organometallic catalysis has long depended on phosphine ligands, PR_3.[1] Only recently have N-heterocyclic carbenes (NHCs) offered the promise of an alternative ligand environment for organometallic catalysis.[2] The precursor imidazolium salts are usually easier to synthesize than are PR_3, but have proved harder to install on the metal—often requiring *n*-BuLi treatment for prior generation of the free carbene.[2]

To be useful as spectator ligands, carbenes must survive the conditions of the catalytic reaction. Once bound to a metal, monodentate carbenes can be reactive, however, undergoing reductive elimination with alkyl groups in some cases.[3] We[4] and others[2,5,6] have therefore been developing chelate carbenes that should better resist degradation under catalytic conditions by benefiting from the chelate effect and stereoelectronic barriers to undesired degradation pathways. Palladium complexes of NHCs have been most studied;[2–4] Rh, also very catalytically active,[1] is rarely studied with polydentate C,C donors.[6]

We now report direct metallation of the imidazolium precursors to give [Rh(bis-carbene)I_2(OAc)] (**2a**–**c**) and their application to catalytic alkene isomerization and transfer hydrogenation of ketones and imines.

N-Alkyl imidazoles readily react with CH_2I_2 in toluene at 120 °C to give the precursor iodide salts **1a**,**b** in high yields (Scheme 1).[7] The *o*-phenylene-bis-imidazolium precursor **1c** has also been prepared by alkylation of *o*-phenylene diimidazole.[8] We now find that **1a**–**c** react with $[(cod)RhCl]_2$ in refluxing MeCN over 16 h in the presence of NaOAc and KI to give **2a**–**c** (46–78% yield).‡ In an alternative route, **1a**–**c** react with $[Rh(OAc)_2]_2$ in refluxing EtCN over 10 h to give **2a**–**c** in *ca.* 50% yield. The air stable red complexes were purified by column chromatography. Mechanisms for these syntheses are not understood and, in view of the redox processes necessarily involved, they may well be complex.



Scheme 1 Synthetic routes: i, $[(cod)RhCl]_2$, NaOAc, KI, EtCN; ii, $[Rh(OAc)_2]_2$, MeCN.

Evidence for a C,C-bidentate chelating bonding mode of the carbene ligand in **2** comes from NMR spectroscopy, which shows that the imidazole rings are symmetry-related. The ^{1}H NMR spectrum of **2b**, for example, reveals one set of signals for the isopropyl groups, and a sharp singlet for the methylene protons around δ 6.2. In the $^{13}C\{^1H\}$ NMR spectrum, the carbene signal is observed as a doublet at δ 154 with coupling constants that are diagnostic for Rh binding ($^1J_{CRh}$ 43 Hz).

One derivative formed crystals suitable for X-ray diffraction.§ Fig 1 shows the structure of **2c**. The carbene is chelating with a ruffled conformation and a bite angle (C1–Rh1–C11) of 92.2(4)°. The Rh–C distances, 1.992(9) and 2.000(10) Å, are normal for Rh–C σ bonds and imply a symmetric ligand coordination mode. The high *trans* effect of the carbenes is evident in the rather long Rh–OAc distances (Rh–O 2.166(6), 2.181(6) Å) compared to those in the parent carboxylate complexes $[Rh(OAc)_2(L)]_2$ (2.01–2.06 Å).[9]

Complex **2b** (0.1 mol%) catalyses the hydrogenation of C=O and C=N groups (eqn. 1) *via* hydrogen transfer from i-PrOH/KOH at 82 °C.[10]

$$RCH{=}E + Me_2CHOH \rightarrow Me_2CO + RCH_2{-}EH \qquad (1)$$

Aryl and alkyl ketones are converted to the corresponding alcohols in good yields (Table 1), though benzophenone, entry 5, required longer reaction times. Pyridine nitrogens do not poison the catalyst: reduction of acetylpyridine occurs readily

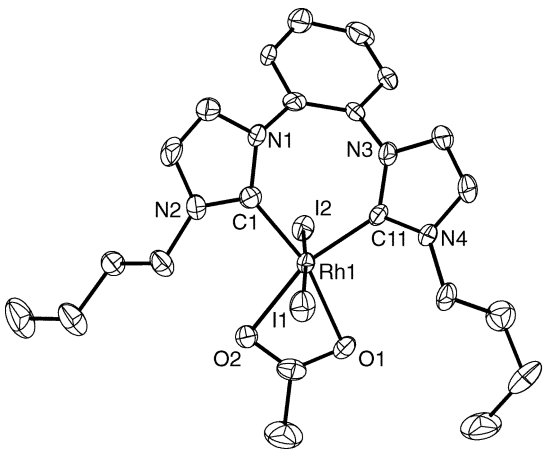


Fig. 1 A view of **2c** (50% probability level, hydrogen atoms omitted for clarity). Pertinent bond lengths (Å) and angles (°): Rh1–C1 1.992(9), Rh1–C11 2.000 (10), Rh1–I1 2.6744(12), Rh1–I2 2.6602(12), Rh1–O1 2.181(6), Rh1–O2 2.166(6); C1–Rh1–C11 92.2(4), C1–Rh1–O1 162.8(3), C11–Rh1–O1 104.7(3), O1–Rh1–O2 60.5(3), I1–Rh1–I2 174.92(4), C1–Rh1–I1 89.6(3), C1–Rh1–I2 95.2(3), C11–Rh1–I1 88.2(3), C11–Rh1–I2 93.2(3).

† Electronic supplementary information (ESI) available: spectroscopic data for the rhodium(III) complexes. See http://www.rsc.org/suppdata/cc/b109491b/

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Table 1 Catalytic transfer hydrogenation using the rhodium(III) catalysts[a]

Entry	Catalyst (mol %)	Substrate	Yield (%)	TON
1	**2b** (0.1)	Acetophenone	>98	1000
2[b]	**2b** (0.1)	Acetophenone	17	170
3	**2b** (0.1)	2-Acetylpyridine	>98	1000
4	**2b** (0.5)	4-Acetylpyridine	>98	200
5	**2b** (0.1)	Benzophenone	72 (89 after 18 h)	890
6[b]	**2b** (0.1)	Benzophenone	0	0
7	**2b** (0.1)	Cyclohexanone	>98	1000
8	**2b** (0.005)	Cyclohexanone	>98	19000
9	**2b** (0.1)	Hexan-3-one	>98	1000
10	**2b** (0.1)	Benzylidene aniline	>98	1000
11	**2b** (0.1)	Benzylidene methylimine	85 (>98 after 18 h)	1000
12	**2c** (0.1)	Benzylidene methylimine	54 (>98 after 36 h)	1000
13	**2c** (0.1)	Benzophenone	78 (95 after 18 h)	950
14[c]	**2c** (0.1)	Benzophenone	80 (>98 after 18 h)	1000
15	None	Acetophenone	<10	—

[a] 2 mmol substrate, 10 mL 0.1 M KOH in i-PrOH, reflux temperature for 10 h, unless stated otherwise; yields determined by ^{1}H NMR or GC; TON = mol product/mol catalyst. [b] At 25 °C. [c] In 2-BuOH as solvent, reflux temperature.

(entries 3 and 4). Cyclic and acyclic aliphatic ketones have been hydrogenated, including ketones with substituents bulkier than methyl groups (entries 7 and 9). Generally, **2b** hydrogenates aliphatic substrates faster than aromatic ones. For example, formation of cyclohexanol from cyclohexanone is complete within 6 h, whereas hydrogenation of benzophenone requires more than 12 h. Attempts to carry out transfer hydrogenation at room temperature had only limited success (entries 2 and 6): acetophenone was converted slowly while benzophenone was unreactive. No aldol condensation byproducts from the acetone were observed. Incubation of the catalyst with KOH/i-PrOH at 82 °C prior to substrate addition did not improve the catalytic performance,[11] so activation of the catalyst system is fast. Control reactions without Rh gave no significant transfer hydrogenation.

Interestingly, **2b** also catalyzes the reduction of imines to the corresponding amines (entries 10 and 11). These N-substituted benzylidene imines react slower than ketones.

The more rigid catalyst system **2c** exhibited similar catalytic activity to **2b**. The reduction of benzylidene methylimine and benzophenone proceeded slightly faster (entries 12 and 13). A 20 °C increase of the reaction temperature by changing the solvent from i-PrOH to 2-BuOH did not improve catalyst performance significantly (entry 14).

Transfer hydrogenation of alkene C=C double bonds failed with our catalysts. Reactions with monosubstituted, terminal olefins (allylbenzene) or disubstituted alkenes (*cis* or *trans*, cyclooctadiene or *trans*-β-methylstyrene) gave no detectable amounts of hydrogenation products under the reaction conditions used for ketone and imine reduction. Attempted reductions of conjugated enones as in 1-phenylbuten-3-one gave a mixture of polymeric products that were poorly soluble in hexane. Clearly, our catalyst systems are not applicable to this type of substrate. Mechanistic studies are in progress but no intermediates have proved isolable so far.

In summary, chelating bis-carbenes can be readily installed on rhodium(III) under mild conditions. The products give robust and air stable catalysts for hydrogen transfer.

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Notes and references

‡ *Typical procedure* for the synthesis of the bis-carbene rhodium(III) complexes: a mixture of methylene-bis(*N*-isopropylimidazolium) diiodide **1b** (488 mg, 1.0 mmol), NaOAc (328 mg, 4.0 mmol), KI (332 mg, 2.0 mmol) and $[RhCl(cod)]_2$ (243 mg, 0.5 mmol) was stirred in EtCN (20 mL) at reflux for 16 h. After cooling, volatiles were removed under reduced pressure and the residue purified by gradient column chromatography. Elution with CH_2Cl_2 gave a $[RhX(cod)]_2$ fraction (X = Cl, I) and subsequent elution with CH_2Cl_2–acetone (3:1) gave **2b** as an orange solid (473 mg, 74%). Analytically pure material was obtained by crystallization from CH_2Cl_2–heptane. Anal. Calc. for $C_{15}H_{23}I_2N_4O_2Rh$ (648.08): C 27.80, H 3.58, N 8.65. Found: C 27.58, H 3.59, N 8.37%.

§ *Crystal data* for **2c**: orange prisms (0.13 × 0.09 × 0.05 mm) M_w = 738.20, monoclinic, space group $P2_1/c$ (no. 14), a = 8.654(3), b = 17.372(6), c = 18.001(6) Å, β = 103.260(8)°, V = 2634.2(16) Å^3, Z = 4, D_c = 1.861 g cm^{-3}, μ = 3.016 mm, Mo–Kα radiation (λ = 0.71073 Å), 11164 reflections measured, 3212 unique, observed reflections ($I > 3.00\sigma(I)$) 280 parameters and converged with unweighted and weighted agreement factors of R = 0.0424, R_w = 0.0940, S = 1.103.CCDC reference number 172875. See http://www.rsc.org/suppdata/cc/b1/b109491b/ for crystallographic data in CIF or other electronic format.

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