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Stable N-functionalised 'pincer' bis carbene ligands and their ruthenium complexes; synthesis and catalytic studies

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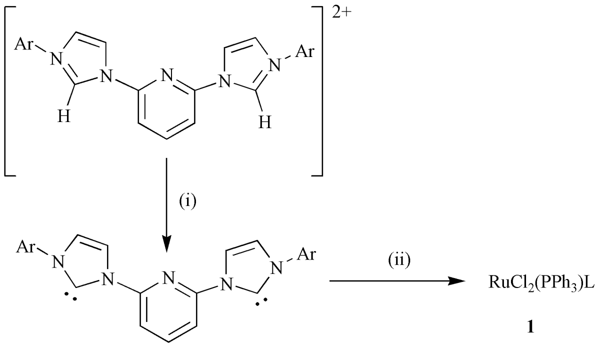
Deprotonation of 2,6-bis(arylimidazolium)pyridine dibromide with $KN(SiMe_3)_2$ gave thermally stable 2,6-bis(arylimidazol-2-ylidene)pyridine, which was further used to prepare ruthenium 'pincer' complexes; the latter show catalytic activity in transfer hydrogenation of carbonyl compounds.

The use of *N*-heterocyclic carbenes (NHCs) in homogeneous catalytic reactions is expanding.[1] Based on the accepted analogy between NHCs and trialkylphosphines[2] many metal complexes have been synthesised and targeted as catalysts for various catalytic reactions. Furthermore, the development of ligand designs incorporating NHCs in addition to other functional groups provides the opportunity for catalyst tuning. In this area we,[3] and others,[4] have studied complexes with mixed donor ligands comprising NHCs linked to nitrogen, phosphorus and oxygen donors. In a recent development we isolated and structurally characterised stable phosphine and pyridine functionalised NHCs.[5] The use of 'functionalised-carbenes-in-a-bottle' allows the synthesis of complexes under mild reaction conditions even by employing thermally unstable and/or base sensitive metal starting materials. Other attractive features of this synthetic approach include, *inter alia*, atom economy, simple purification and possible parallel catalyst testing involving free carbenes. In this communication we describe the first isolation and structural characterisation of chelating 'pincer' NHCs and their use in the synthesis of ruthenium complexes, which are not accessible using *in situ* deprotonation methods either by mild (OAc^-) or organometallic bases (potassium or lithium alkoxides, amides *etc*.).

Interaction of 2,6-[(*o*-dialkyl)phenylimidazolium]pyridine dibromide with two equivalents of $KN(SiMe_3)_2$ in THF at −10 °C (Scheme 1) afforded the 2,6-[(*o*-dialkyl)phenylimidazolylidene]pyridine, **L**,† in 70–80% yields after crystallisation from toluene. This reaction has been run successfully up to *ca* 3 g scale. The off-white crystalline product can be handled as a solid under nitrogen at room temperature for hours without any noticeable decomposition and is indefinitely stable at −30 °C.



L

Ar=2,6-$Pr^i_2C_6H_3$, **L^1**,
Ar=2,6-$Me_2$4-$Bu^tC_6H_2$, **L^2**

Scheme 1 *Reagents and conditions*: (i) $KN(SiMe_3)_2$, THF, −10 °C; (ii) $RuCl_2(PPh_3)_3$, THF.

The structure of **L^1** was determined by diffraction methods, (Fig 1).‡ The molecule is strictly planar adopting a conformation in which the carbene and the pyridine lone pairs are mutually *anti*, possibly in order to minimise lone pair repulsions. **L^1** is the first example of a structurally characterised dicarbene and supports the view that free multidentate NHCs are stable and isolable molecules provided that dimerisation reactions are blocked by ring strain and/or electronic factors.

A variety of bis carbenes supported on aromatic or aliphatic backbones have now been isolated and fully characterised and will be the subject of a future publication.

L can be used in mild and clean ligand substitution reactions in polar nonprotic solvents providing high yields of 'pincer' bis carbene complexes. For example, reaction of one equivalent of **L^1** with $RuCl_2(PPh_3)_3$ in THF, gave the ruthenium bis carbene complex **1** as an orange air stable crystalline solid.† The structure of **1** is shown in Fig. 2. The chelate system occupies three meridional sites and the two chlorides are mutually *cis*. Ruthenium complexes with monodentate imidazolin-2-ylidenes and imidazol-2-ylidenes have been reported.[6] This is the first example of a chelating bis carbene. In solution in non-coordinating solvents there is partial dissociation of PPh_3 as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. In coordinated solvents (MeCN) there is rapid substitution of the coordinated chlorides by solvent.

'Pincer' bis carbene palladium complexes, were recently reported by us[3c] and others;[4d,7] they were prepared from silver carbene complexes or by *in situ* deprotonation methods. Attempts to prepare **1** using these protocols gave intractable mixtures. Analogous phosphine and amine pincers were reported by Osborn,[8a] van Koten[8b] and others, and exhibit rich and diverse chemistry.

In a preliminary study, complex **1** catalyses the hydrogenation of C=O and C=N groups by hydrogen transfer from isopropyl alcohol in the presence of $KOBu^t$ or $KOPr^i$. The reactions are slow at room temperature but proceed at good rates at 55 °C or 80 °C. Representative catalytic data are given in Table 1. The catalyst system hydrogenates aliphatic ketones faster that aromatic ones and imines. Although conditions have

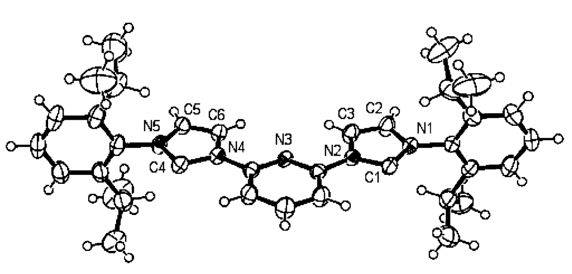


Fig. 1 Molecular structure of **L^1**. Thermal ellipsoids shown at 50% probability. The asymmetric unit contains one molecule of THF and one molecule of toluene. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.36(3), C(1)–N(2) 1.37(2), C(2)–C(3) 1.33(3), C(2)–N(1) 1.39(2), C(3)–N(2) 1.39(3), C(11)–N(3) 1.33(2), C(11)–N(2) 1.43(2). Dihedral angle C(1)–N(2)–C(11)–N(3) 177.5, C(7)–N(3)–C(4)–N(4) 179.7.

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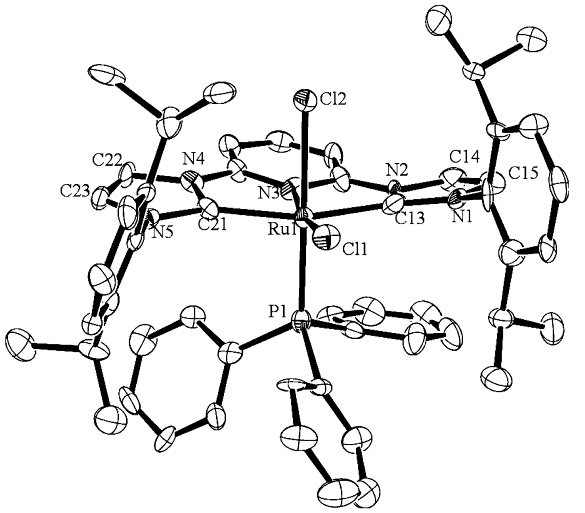

Fig. 2 Molecular structure of **1**. Thermal ellipsoids shown at 50% probability. The asymmetric unit contains two molecules and two molecules of dichloromethane. Selected bond lengths (Å): C(13)–Ru(1) 2.025(8), C(21)–Ru(1) 2.028(8), N(3)–Ru(1) 1.971(7), Cl(1)–Ru(1) 2.424(2), Cl(2)–Ru(1) 2.478(2), Ru(1)–P(1) 2.318(2).

Table 1 Selected results of transfer hydrogenation catalysed by **1**[a]

Substrate	Temper-ature/°C	Time/h	Catalyst/mol %	TON
Cyclohexanone	25	12	0.1	150
Cyclohexanone	55	12	0.050	1900
Cyclohexanone	55	20	0.010	8800
Acetophenone	55	20	0.015	2500
Acetophenone	80	12	0.015	4000
Benzylidene aniline	55	20	0.015	4200

[a] Amounts: 5×10^{-3} M catalyst, 50 mmol substrate, 0.5 g (4.5 mmol) Bu^{t}OK, in Pr^{i}OH. Yields determined by GC of the isolated product mixture.

not yet been optimised, it is obvious that the activity is comparable to that observed with phosphine and amine arylpincer ruthenium complexes,[10] but lower than the aminoalcohol based systems of Noyori.[9] Furthermore, these data show the viability of ruthenium transfer hydrogenation catalysts stabilised by NHCs operating in protic solvents.[11] The stability provided by the chelate ligand, the availability of two *cis* reactive sites and the potential for electronic/coordinative unsaturation are possible reasons for the activity observed. Further mechanistic studies on this reaction are in progress.

In summary, the isolation of free 'pincer' type bis carbene ligands has opened new and easy synthetic routes to a variety of complexes with wide scope for functionalisation and catalyst optimisation and tuning. The synthesis of other 'pincer' complexes with catalytically important metals using this methodology is under way.

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Notes and references

† Spectroscopic data for **L¹**: NMR (C_6D_6), ^{1}H, δ 1.2 and 1.4 [two doublets, 24H, diastereotopic (CH_3)CH], 3.0 [septet, 4H, (CH_3)CH], 6.7 (d, 2H, imidazol-2-ylidene), 7.2–7.5 (m, 7H, aromatic and pyridine ring protons), 8.2 (d, 2H, imidazol-2-ylidene), 8.6 (d, 2H, pyridine ring protons). ^{13}C{^{1}H}, 24.0 and 24.4 [(CH$_3$)$_2$CH], 28.6 [(CH$_3$)$_2$$C$H], 111.7, 116.2, 122.8, 123.8, 129.2, 138.7, 140.7, 146.2, and 152.6 (aromatic, pyridine and carbene ring carbons), 219 (carbene C).

For **L²**: NMR (C_6D_6), ^{1}H, δ 1.3 [s, 18H, (CH_3)$_3$C], 2.2 (s, 12H, *o*-CH_3), 6.4 (d, 2H, imidazol-2-ylidene), 7.2–7.3 (m, 5H, aromatic and pyridine ring protons), 8.2 (d, 2H, imidazol-2-ylidene), 8.6 (d, 2H, pyridine ring protons). ^{13}C{^{1}H}, 18.6 [(CH$_3$)$_3$C], 31.6 (*o*-CH$_3$), 34.5 [(CH$_3$)$_3$$C$], 111.2, 116.6, 121.6, 125,6, 135.2, 139.0, 140.8, 151.0, 152.8, (all aromatic carbons), 220 (carbene C).

For **1**: NMR (CD_2Cl_2), ^{1}H 0.6, 0.7, 0.9 and 1.0 [all doublets, 24H, (CH_3)$_2$CH] 2.3 and 2.7 [4H, septet, (CH_3)$_2$CH)], 6.8–9.2 (multiplets, 28H, aromatic). 31P{1H}: δ 10.29.

‡ *Crystal data* for **L¹**: $C_{42.5}$ H_{53} N_5 O_1, clear needles (0.01 × 0.005 × 0.005 mm), *Mw* 649.9, Orthorhombic, *Fdd*2 (No. 43), a = 29.947(2) Å, b = 48.760(4) Å, c = 10.9022(9) Å, $a = ß = \gamma = 90°$, V = 15920(2) Å^3, Z = 16, D_c = 1.085 mg m^{-3}, μ = 0.066 mm^{-1}, λ = 0.6875 Å, T = 150 K, Total reflections = 17293, unique reflections = 7126 (R_{int} = 0.0469), Final R indices [$I > 2s(I)$] R = 0.1115, R_w = 0.3259 (all data). These were collected at the Daresbury SRS on station 9.8 due to the extremely small size of the crystals.

Crystal data for **1**: C_{108} H_{116} Cl_8 N_{10} P_2 Ru_2, orange plates (0.06 × 0.04 × 0.01 mm), *M*w 2101.79, Orthorhombic, *Pca*2*₁* (No. 29), a = 17.9597(5) Å, b = 19.2091(6) Å, c = 28.7358(10) Å, $a = ß = \gamma = 90°$, V = 9913.6(5) Å^3, Z = 4, D_c = 1.408 mg m^{-3}, μ = 0.607 mm^{-1}, λ = 0.71073 Å, T = 150 K, Total reflections = 23471, unique reflections = 9624, Final R indices [$I > 2s(I)$] R = 0.0455, R_w = 0.0986 (all data). This compound was refined as racemic twin [flack parameter 0.48(4)]. CCDC 182353 and 182354. See http://www.rsc.org/suppdata/cc/b2/b202814j/ for crystallographic files in .cif or other electronic format.

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