Synthesis of the Ruthenium Imido Complexes, $[Ru(\eta\text{-}C_6H_6)(N\text{-}2,6\text{-}R_2C_6H_3)]_2$ (R = Pr^i or Me), and the Crystal Structure of $[Ru(\eta\text{-}C_6H_6)(N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)]_2$

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Ruthenium imido complexes, $[(\eta\text{-}C_6H_6)Ru(N\text{-}2,6\text{-}R_2C_6H_3)]_2$ (R = Pr^i **1**, Me **2**), have been synthesised by the room temperature reaction of $[(\eta\text{-}C_6H_6)RuCl_2]_2$ with 2 equiv. of $LiNH(2,6\text{-}R_2C_6H_3)$ and **1** has been shown by single-crystal X-ray diffraction to be a symmetrical, imido-bridged dimer containing a bent Ru_2N_2 bridge.

The imido ligand has received considerable attention in recent years, primarily because of its ability to stabilise high metal oxidation states by multiple electron donation.[1] However, relatively few studies have focused on imido complexes of the later transition elements.[2] Recently we have been studying complexes containing the sterically demanding 2,6-diisopropylphenylimido ($N\text{-}2,6\text{-}Pr^i{}_2C_6H_3$) ligand coordinated to Mo, W, Re and Os[3a–d] and have demonstrated its utility in synthesising active, well-defined, alkene metathesis catalysts.[4] In order to extend our studies to other, later transition metals we sought access to imido complexes of ruthenium.[5]

Since $[(\eta\text{-}C_6H_6)MCl_2]_2$ (M = Ru, Os) complexes are isoelectronic with $[(C_5Me_5)MCl_2]_2$ (M = Rh, Ir) complexes, we felt that they might react to give complexes analogous to recently discovered[2d] $(C_5Me_5)M(NBu^t)$ complexes [(eqn. (1)]. This strategy was successful employing aryl-substituted amides but not $LiNHBu^t$, which gives an intractable mixture of products under analogous conditions. Although formation of **1** and **2** is quantitative by NMR, the isolated yields (not yet optimised) are moderate (48% **1**, 77% **2**) due to difficulties in separating the aniline byproducts. We believe that $(\eta\text{-}C_6H_6)RuCl(NHAr)$ is likely to be formed first and then either dehydrohalogenated by the second equiv. of LiNHAr or attacked to form $(\eta\text{-}C_6H_6)Ru(NHAr)_2$, which then loses NH_2Ar.

$$[(\eta\text{-}C_6H_6)RuCl_2]_2 + 4\,LiNHAr \xrightarrow{Et_2O} 2\,(\eta\text{-}C_6H_6)Ru(NAr) + 4\,LiCl + 2\,NH_2Ar \quad (1)$$

$$Ar = 2,6\text{-}Pr^i{}_2C_6H_3\ \mathbf{1},\ 2,6\text{-}Me_2C_6H_3\ \mathbf{2}$$

Both **1** and **2** are deep-green, air-sensitive, crystalline compounds which dissolve readily in aromatic and ethereal solvents, but significantly less readily in pentane. Analytical and spectroscopic data† for **1** and **2** support the proposed

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† *Selected spectroscopic data*: **1** ^1H NMR (C_6D_6) δ 7.3–7.25 (m, 6H, Ar-$H_{m/p}$), 4.42 (s, 6H, C_6H_6), 3.58 (sp, *J* 6.8, 4H, Pr^i-C*H*), 1.31 (d, *J* 6.8, 24H, Pr^i-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 166.99 (C_{ipso}), 137.23 (C_o), 123.55 ($C_{p/m}$), 123.18 ($C_{p/m}$), 78.69 (C_6H_6), 26.83 (Pr^i-*C*H), 25.48 (Pr^i-*C*H_3). Mass spectrum (EI) *m/z* 354, M^+, ^{102}Ru). **2** ^1H NMR (C_6D_6) δ 7.3–7.1 (m, 6H, Ar-$H_{m/p}$), 4.26 (s, 6H, C_6H_6), 2.27 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 169.45 (C_{ipso}), 125.61 ($C_{m/p}$), 122.17 ($C_{m/p}$), 79.13 (C_6H_6), 19.30 (CH_3). Mass spectrum (EI) *m/z* 597, M^+, ^{102}Ru). Satisfactory elemental analyses have been obtained for **1** and **2**.

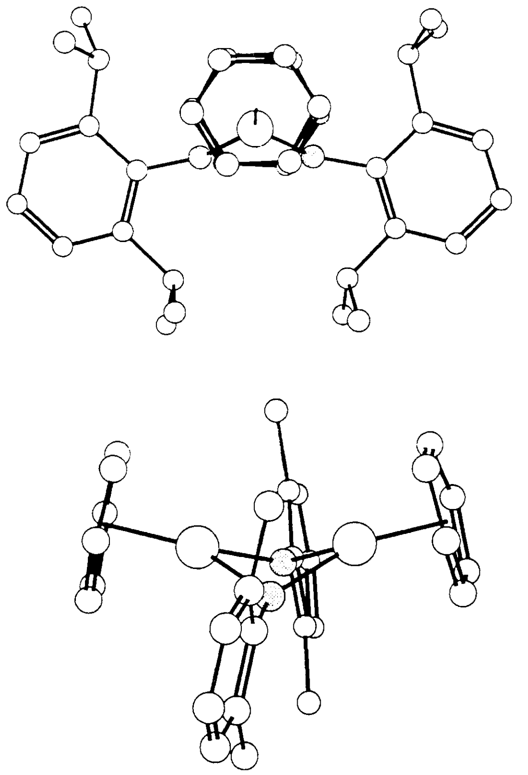

Fig. 1 Two views of the structure of $[Ru(\eta-C_6H_6)(N-2,6-Pr^i{}_2C_6H_3)]_2$. (The isopropyl methyl groups have been omitted from the bottom view.)

composition. Mass spectra of **1** reveal a peak at *m/z* 354 corresponding to $[(\eta-C_6H_6)Ru(N-2,6-Pr^i{}_2C_6H_3)]^+$, while a mass spectrum of **2** shows clearly a peak for a dimer at *m/z* 596.

A single-crystal X-ray diffraction study of **1**‡ reveals that the complex is a dimer with symmetrically bridging imido ligands (Fig. 1). The ruthenium atoms are separated by 2.777(3) Å, a distance that is significantly shorter than that found in $[(\eta-C_5H_5)_2Ru_2(OMe)_2$,[6] 2.961(1) Å] and within the range observed for Ru–Ru single bonds (*ca.* 2.74–2.86 Å).[6] The Ru–N distances are identical [Ru(1)–N(1) = 1.96(1) Å; Ru(1)–N(2) = 1.97(1) Å]. The aryl planes are oriented approximately perpendicular to their respective Ru_2N planes and the coordination around each nitrogen atom is planar, suggesting that the nitrogen lone pairs are involved in delocalised bonding between metal centres. Most significant perhaps is the bent M_2N_2 bridge [dihedral angle Ru(1)–Ru(2)–N(1)/Ru(1)–Ru(2)–N(2) = 128.76°], a feature that is often associated with d^n systems where *n* is odd, and one that results in metal–metal bonding.[7] When *n* is even, the requirement for M–M bond formation is less stringent and a planar bridge is normally observed.[8] Exceptions are $Rh_2Cl_2(CO)_4$[9] and $(\eta-C_5H_5)_2Ru_2(OMe)_2$.[6] In these cases *ab initio* calculations have suggested that no M–M bond is formed and that bending is the result of second order Jahn–Teller effects.[6a] A similar explanation may be appropriate for **1**, where, upon bridge bending, the filled, π-bonding molecular orbital illustrated (Fig. 2) is significantly stabilised with respect to a planar Ru_2B_2 arrangement. Thus, the relatively short Ru–Ru separation may primarily be a result of the short Ru–N bond lengths. We believe **2** to possess a similar dimeric structure in the solid state on the basis of mass spectral data mentioned above.

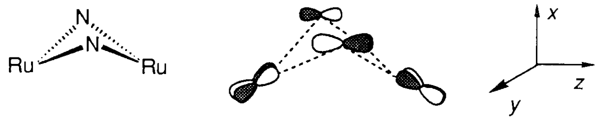

Fig. 2 A description of the bonding in the Ru_2N_2 bridge in **1**

Preliminary reactivity studies suggest that **1** and **2** contain relatively non-labile arene ligands; for example, no exchange of C_6H_6 for C_6D_6 is observed after heating **1** to 75 °C for 9 h or upon photolysis with a medium pressure mercury lamp for 3 h. Although **2** does not react with tetrahydrofuran, pyridine or PMe_3 in refluxing benzene, it does react with HCl, water, dichloromethane, methyl iodide, and iodine. Full characterisation of these products is currently in progress.

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‡ *Crystal data* for $C_{18}H_{23}NRu$: *M* = 354.46, monoclinic, $P2_1/n$, *a* = 9.975(8), *b* = 18.93(1), *c* = 18.733(8) Å, β = 91.36(5)°, *U* = 3536(4) Å^3, *Z* = 8, D_c = 1.444 g cm^{-3}, λ = 0.71069 Å, μ = 8.67 cm^{-1}, *F*(000) = 1576, *T* = 296 K. The data were collected on a Rigaku AFC6R diffractometer. The structure was determined *via* Patterson methods; the final cycle of full matrix least-squares refinement was based on 3816 reflections with $2\theta < 49.9°$, $I > 3\sigma(I)$. The structure was found to be dimeric. One half of a pentane molecule whose central atom was located upon a special position was found in the unit cell; this fragment could not be refined anisotropically. All other atoms were refined anisotropically. The final *R* = 0.050, R_w = 0.065. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See notice to Authors, Issue No. 1.