(η^6-*p*-cymene)Ru≡N(2,4,6-tri-*tert*-butylphenyl): A Monomeric Ruthenium(II) Complex containing a Terminal Imido Ligand

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The first example of a terminal d^6 imido ruthenium complex, (η^6-*p*-cymene)Ru≡N(2,4,6-tri-*tert*-butylphenyl), is prepared and structurally characterised.

The area of transition metal imido chemistry has experienced dramatic growth in recent years.[1,2] Stable terminal imido complexes are known for many of the transition metals and even some of the actinides.[3] The first organoimido complex reported was $Os(=NBu^t)O_3$[4] and since this initial report the number and variety of osmium–imido compounds has continued to increase every year.[2] In contrast, ruthenium–imido chemistry[5] has developed slowly with only one example of a structurally characterised terminal imido complex known.[6] While stable, well-characterised terminal imido complexes of ruthenium are rare, several compounds containing bridging imido ligands have been reported.[7–9] One notable example is the dimeric complex $(C_6H_6)Ru(\mu^2\text{-NAr})_2Ru(C_6H_6)$,[8] which contains two bridging imido ligands. The structure of this complex is somewhat surprising as the related osmium complexes are monomeric, containing terminal imido ligands as shown in Fig. 1.[10] Recently, it has become clear that it is possible to convert imido ligands from bridging to terminal by increasing the steric congestion about the metal centre.[11] In general, this is most easily achieved by increasing the size of the functional group on the imido ligand. Herein, we report the synthesis and structures of the first example of a terminal mono-imido complex of ruthenium, (η^6-*p*-cymene)Ru≡NAr′, and the related dimeric complex [(η^6-*p*-cymene)RuNAr]$_2$ (Ar = 2,6-diisopropylphenyl, Ar′ = 2,4,6-tri-*tert*-butylphenyl).

The reaction of four equivalents of LiNHAr with [(η^6-*p*-cymene)RuCl$_2$]$_2$ **1** in THF under conditions similar to those previously reported,[8,11] results in the formation of a deep-green solution. Upon workup, deep blue-green crystals of the composition [(η^6-*p*-cymene)RuNAr] **2** are obtained, (Scheme 1).† Previous work[8] has indicated the difficulties associated with the interpretation of the spectroscopic data in this type of complex. Despite the fact that the analogous osmium complex (η^6-*p*-cymene)Os≡NAr is reported to be monomeric[10] it was not possible to rule out a dimeric complex, such as (η^6-*p*-cymene)-Ru(μ^2-NAr)$_2$Ru(η^6-*p*-cymene). The only conclusive method for determining the nature of **2** is a single-crystal X-ray determination.‡ Suitable crystals of **2** were obtained by evaporation of a benzene–hexamethyldisiloxane solution. The refined structure, depicted in Fig. 2, confirms that **2** indeed exists as the dimeric bridged imido complex, (η^6-*p*-cymene)Ru(μ^2-NAr)$_2$Ru(η^6-*p*-cymene) **2**. The structure of **2** is very similar to that of the previously reported complex $(C_6H_6)Ru(\mu^2\text{-NAr})_2Ru(C_6H_6)$,[8] in

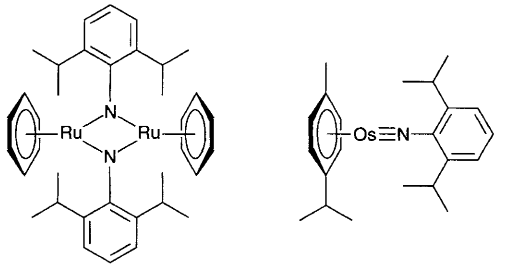
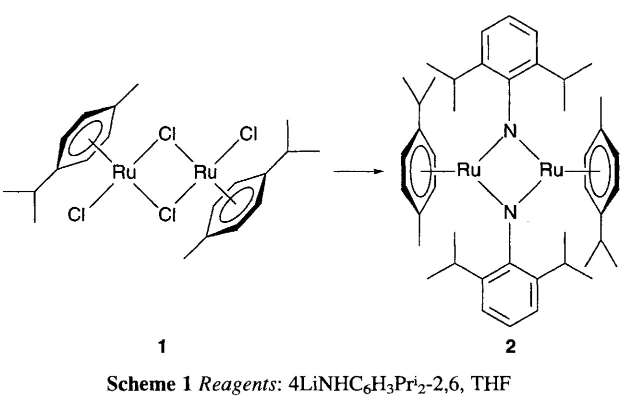


Fig. 1 The two known limiting geometrical forms for the complexes of the formulation (η^6-arene)M(NR) (M = Ru or Os)



1 **2**

Scheme 1 *Reagents*: 4LiNHC$_6$H$_3$Pr$^i_2$-2,6, THF

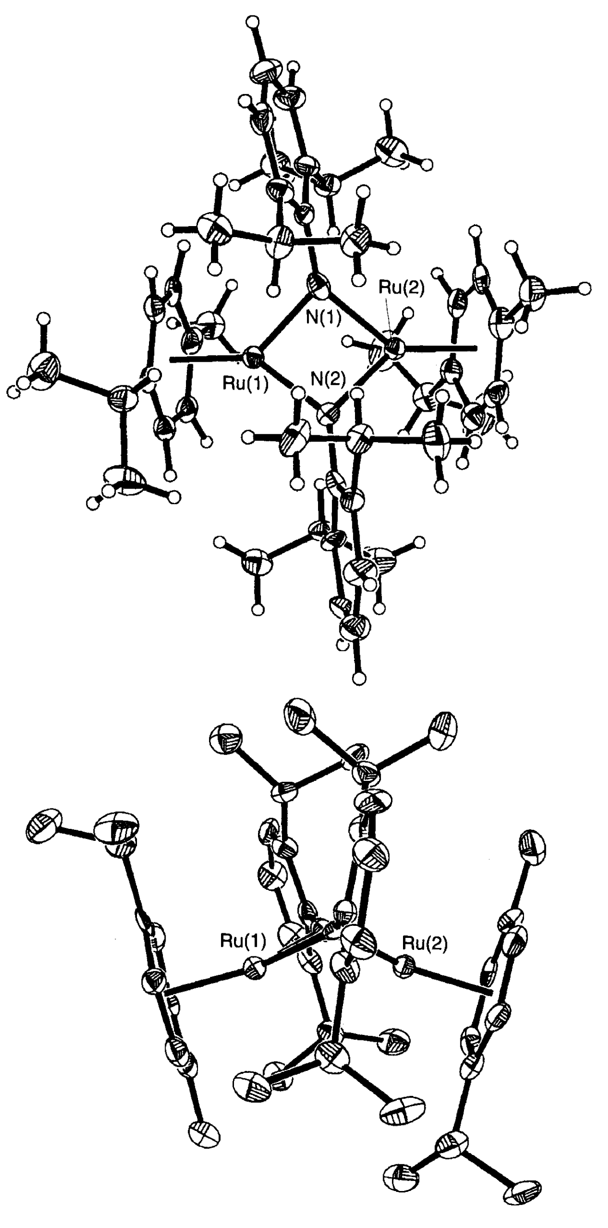
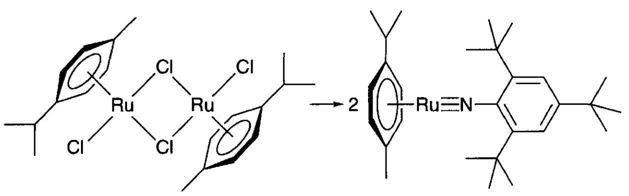


Fig. 2 Structure of **2**: the hydrogen atoms have been omitted in the lower view for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 1.959(8), Ru(1)–N(2) 1.977(7) Ru(2)–N(1) 1.985(8), Ru(2)–N(2) 1.976(8), Ru(1)–Ru(2) 2.7515(12), Ru(1)–N(1)–Ru(2) 88.5(3), Ru(1)–N(2)–Ru(2) 88.2(3), N(1)–Ru(1)–N(2) 78.5(3), N(1)–Ru(2)–N(2) 77.9(3).

that there is a distinct deformation of the ruthenium–nitrogen plane. The nitrogen atoms are bent some 1.188(8) Å above an ideal 'flat' ruthenium–nitrogen plane. Also the ruthenium–ruthenium distance, 2.7515(12) Å, is short and falls within the range of known Ru–Ru bonds. This is more likely due to the geometry imposed by the bridging imido ligands than the presence of a Ru–Ru bond. This suggestion is supported by the appearance of only one signal for the isopropyl groups on the μ-NAr ligands indicating rapid inversion in solution. Clearly, the steric pressure around the metal centre must be increased even more to isolate a terminal imido complex, of the type (η^6-arene)M(NR).

While NAr is generally considered a sterically demanding ligand, NAr′ is more demanding still.[3] The reaction of four equivalents of LiNHAr′ with [(η^6-*p*-cymene)RuCl$_2$]$_2$ **1** in THF once again yields a deep-green solution and a complex that has the formulation [(η^6-*p*-cymene)RuNAr′] **3**, (Scheme 2). The physical and spectroscopic data for **3** are very similar to that of **2** and as before the only conclusive method for determining the structure of **3** was single-crystal X-ray analysis.§ Suitable crystals of **3** were obtained from the evaporation of a benzene–hexamethyldisiloxane solution. The compound crystallises in the space group $P\bar{1}$ with two independent molecules in the asymmetric unit. The molecular geometry, shown in Fig. 3, clearly indicates that **3** is a monomeric complex containing a terminal imido ligand. The averaged Ru–N–C angle is approximately linear at 177.8(4)°. The averaged Ru≡N distance, at 1.753(3) Å is consistent with the mutilple bond character expected of a terminal imido ligand[1,2] and compares well with the only other structurally characterised terminal imido complex of ruthenium, Ru(=NAr)$_2$(PMe$_3$)$_2$ at 1.785(6) Å.[6] The Ru–N in distance in **3** is also similar to that observed in the related osmium complex η^6(C$_6$Me$_6$)Os≡NBu^t at 1.737(3) Å.[10]

These results suggest that steric factors can control the structure of (η^6-arene)M(NR) (M = Ru or Os) complexes.[8,9] However, the dimeric nature of **2** raises the question, why is the analogous osmium complex,[10] (η^6-*p*-cymene)Os≡NAr monomeric? We intend to extend the range of structurally characterised (η^6-arene)Ru≡NR complexes in an attempt to determine the exact constraints necessary to prevent the formation of bridged imido dimers and to explain the apparent discrepancies between the osmium and ruthenium chemistry.



1 **3**

Scheme 2 *Reagents*: 4LiNHC$_6$H$_2$Bu$^t_3$-2,4,6, THF

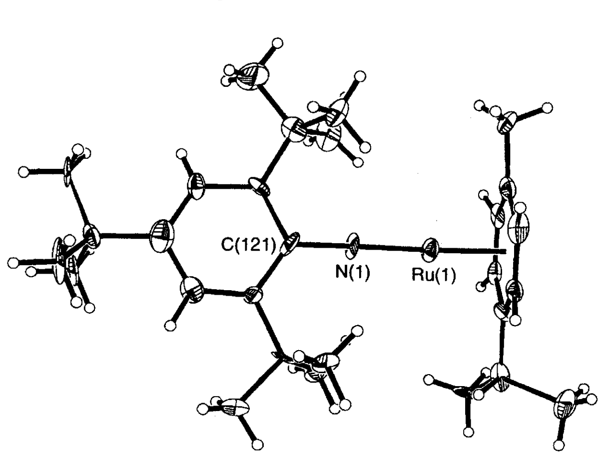


Fig. 3 Structure of **3** (molecule 1): selected bond lengths (Å) and angles (°): Ru(1)–N(1) 1.751(14), N(1)–C(121) 1.39(2), Ru(1)–N(1)–C(121) 178.5(12)

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Footnotes

† All new compounds were fully characterised by elemental analyses, ^{1}H and ^{13}C NMR.

‡ *Crystal data* for (η^6-*p*-cymene)Ru(μ^2-NAr)$_2$Ru(η^6-*p*-cymene) **2**: formula C$_{48}$H$_{60}$N$_2$Ru, M = 821.10; space group $P2_1/c$; a = 19.786(14), b = 10.238(9), c = 19.466(13) Å, β = 99.47(6)°, U = 3889.5 (14) Å^3, Z = 4, D_c = 1.402 Mg m^{-3}; Siemens P4 diffractometer; 203 K; Mo-Kα radiation (λ = 0.71073 Å); scan method 2θ–θ; data collection range 2.09–24.02°; total number of data measured 7408; number of independent reflections 6088 (R_{int} = 14.36% due to extremely air-sensitive poorly formed crystal). The structure was solved by direct methods and refined by a full-matrix least-squares procedure (all non-hydrogen atoms anisotropic), using SHELXL-93[12] and $|F^2|$, to a conventional R of 0.064 for the 3060 reflections [$I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Crystal data* for (η^6-*p*-cymene)Ru≡NAr′ **3**: formula C$_{25}$H$_{42}$NRu, M = 494.7; space group $P\bar{1}$; a = 10.445(4), b = 13.723(5), c = 20.101(6) Å, α = 90.51(3), β = 98.69(4), γ = 112.26(3)°, U = 2629 (2) Å^3; Z = 4; D_c = 1.250 Mg m^{-3}; Siemens P4 diffractometer; 203 K; Mo-Kα radiation (λ = 0.71073 Å); scan method 2θ–θ; data collection range 2.06–22.51°; total number of data measured 5994; number of independent reflections 5550 (R_{int} = 18.75% due to extremely air-sensitive poorly formed crystal). The structure was solved by direct methods and refined by a full-matrix least-squares procedure (all non-hydrogen atoms anisotropic), using SHELXL-93[12] and $|F^2|$, to a conventional R of 0.0810 for the 3566 reflections [$I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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