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Computational Study of the *C*- and *N*-Bound Tautomers of [Ru(Cl)(H)(CO)-(PPh_3)$_2$(I*i*PrMe$_2$)] (I*i*PrMe$_2$ = 3-Isopropyl-4,5-dimethylimidazol-2-ylidene)

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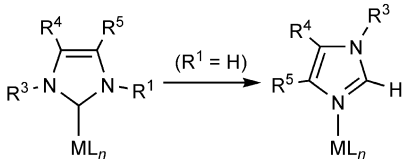
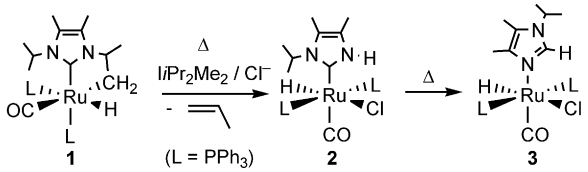
Density functional theory calculations have been used to study the factors controlling the relative energies of the *C*-bound (**2**) and *N*-bound (**3**) tautomers of [Ru(Cl)(H)(CO)-(PPh_3)$_2$(I*i*PrMe$_2$)] (I*i*PrMe$_2$ = 3-isopropyl-4,5-dimethylimidazol-2-ylidene) reported by Whittlesey and co-workers (*J. Am. Chem. Soc.* **2006**, *128*, 13702). The calculations indicate that the *N*-bound form is more stable. Further analysis reveals the presence of a CO ligand *trans* to the C/N binding site is a key factor in determining the greater stability of the *N*-bound form. This preference is further enhanced by the bulky *i*Pr substituent at the N3 position. The calculations predict that the *C*-bound tautomer will be favoured with NHC ligands that feature a bulky C5 substituent in combination with small groups at N3 and C4. Thus [Ru(Cl)(H)(CO)(PPh_3)$_2$-(NHC)] complexes where NHC = 5-R-imidazol-2-ylidene or 3-Me-5-R-imidazol-2-ylidene (R = *t*Bu, Ph) are predicted to be more stable as the *C*-bound form. Five-coordinate square-pyramidal species formed by loss of a CO or Cl ligand from **2** and **3** show an increased preference for the *C*-bound form. Indeed, when the C/N binding site is *trans* to a vacant site the *C*-bound tautomer becomes the more stable species.

Introduction

N-heterocyclic carbenes (NHCs) have become extremely popular supporting ligands in organometallic chemistry and homogeneous catalysis.[1–3] The success of these ligands is founded primarily on their ability to act as powerful σ-donors[4–5] as well as the possibility of fine-tuning ligand electronic and steric properties through variation of substituents around the ring, especially at the N1 and N3 positions (see below). The most commonly employed NHCs feature alkyl or aryl groups at these sites. The behaviour of such NHCs as ligands is, however, not always innocent and many examples have now been reported where potentially undesirable ligand-based processes occur.[6] Prominent among these are C–H[7–8] and C–C[8] bond activation reactions within the R^1/R^3 substituents and even cleavage of the N_{ring}–$C_{substituent}$ bond.[9–10]



A particularly intriguing class of NHC-based reaction has been observed when one or both of R^1 and R^3 = H. In such cases tautomerism between the *C*-bound NHC to an *N*-bound imidazole may occur. The reverse process, NHC formation through N- to C-tautomerism of an imidazole ligand was reported by Taube as early as 1974 for the [Ru(NH_3)$_5$(imidazole)]$^{2+}$ system,[11] and other examples have since been published.[12] However, it was only relatively recently that the direct observation of C- to N-tautomerism of an NHC ligand was reported by Whittlesey and co-workers.[10] They demonstrated that heating cyclometalated [Ru(H)(CO)(PPh_3)$_2$(I*i*Pr$_2$Me$_2$′)] (**1**) (where I*i*Pr$_2$Me$_2$ = 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene), in THF in the presence of a chloride source and free I*i*Pr$_2$Me$_2$ resulted in initial C–N bond cleavage and loss of propene to form complex **2** featuring an asymmetrically substituted NHC ligand. Extended heating (still in the presence of I*i*Pr$_2$Me$_2$) then led to complete conversion to the *N*-bound tautomer, **3**, indicating this to be the more thermodynamically stable form. Further examples of C- to N-tautomerism have subsequently been reported.[9b,9c]



The factors controlling the energetic balance between the *C*-bound NHC and the *N*-bound imidazole have been explored by Sini, Eisenstein and Crabtree.[13] These workers employed density functional theory (DFT) calculations and showed the *C*-bound form becomes more accessible when

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(i) the ligand *trans* to the C/N-binding site has a low *trans* influence; (ii) heavier 2nd or 3rd row transition metal fragments of strongly π-basic character are employed; and (iii) H-bond acceptors can stabilize the acidic N–H bond(s) exposed in the *C*-bound tautomers. Frenking has also used DFT calculations to compare simple NHC and imidazole ligands and showed the former to be significantly stronger σ-donors.[14]

In addition to interconversion between imidazole and NHC ligands, the metal-mediated tautomerism of several other N-heterocyclic ligands to their *C*-bound carbenic forms has also been observed. Examples with pyridines and phenanthroline,[15] quinolines[16] and benzodiazapenes[17] have all been reported. In many cases the presence of a substituent in the 2-position was found to be important (although not always essential[15b]) in promoting N- to C-tautomerism. H-Bonding to the N-H group of the *C*-bound form is also a common feature that may stabilise the *C*-bound tautomer.[15f,16a] N- to C-tautomerism has also been proposed as a key step in Rh-catalysed C–C coupling reactions of various N-heterocyclic substrates[18] and computational studies on the mechanism of the N- to C-interconversion in some of these systems have also been reported.[16c,18c]

In this paper, we employ DFT calculations to study the factors that control the energetic preference for the *N*-bound tautomer in the Whittlesey system. We shall initially consider the full molecules **2** and **3** and demonstrate that **3** is indeed computed to be the more stable form. A series of calculations will then study the effects of the immediate metal environment on the energy difference between **2** and **3**. Further calculations will then probe the effect of changing the various ligand substituents. The results allow us to suggest alternative NHC ligands which are predicted to be more stable as the *C*-bound tautomer when bound to the {Ru(Cl)(H)(CO)(PPh_3)$_2$} fragment.

Results and Discussion

Computed Structures of 2 and 3

The computed structure of [Ru(Cl)(H)(CO)(PPh_3)$_2$-(I*i*PrMe$_2$)] (**2**) (where I*i*PrMe$_2$ = 3-isopropyl-4,5-dimethylimidazol-2-ylidene), is shown in Figure 1 and that of its *N*-bound tautomer, **3**, in Figure 2. In each case good agreement with the experimental structures derived from X-ray diffraction studies is seen, with the Ru–C2 and Ru–N1 bond lengths in **2** and **3** respectively being well reproduced. Elsewhere the Ru–P and Ru–Cl distances are slightly overestimated in the calculations, although the percentage error amounts to less than 2%. One feature of **2** is a short N1–H1···Cl contact with a calculated distance of 2.19 Å and, possibly related to this, a tilting of the NHC ligand toward Cl in **2** (Ru–C2–N1 = 120.3°; Ru–C2–N3 = 135.8°). In **3** the computed C2–H1···Cl contact of 2.42 Å suggests a degree of interaction is retained, albeit weaker than the N1–H1···Cl interaction in **2**. In this case a lesser degree of tilting is seen, with a small difference in the Ru–N1–C2/C5 angles being computed (122.6° and 130.6°). The factors behind these tilting distortions will be explored in more detail below.

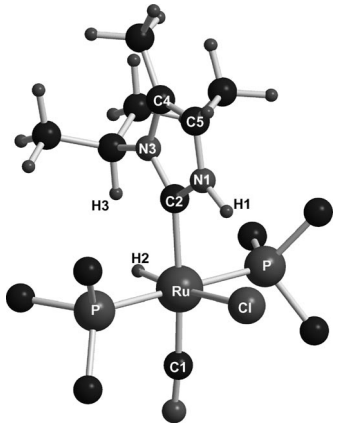


Figure 1. Computed structure of **2** with phenyl groups truncated at the *ipso* carbon atoms. Key distances [Å] and angles (with equivalent experimental data in italics[10]): Ru–C1 1.88/*1.884(2)*; Ru–C2 2.14/*2.1282(18)*; Ru–P(av) 2.38/*2.3540(7)*; Ru–Cl 2.61/*2.5666(5)*; Ru–H2 1.59; N1–H1 1.04; H1···Cl 2.19; P–Ru–P 179.8°/*174.358(17)*°; C1–Ru–C2 173.3°/*173.09(7)*°; Ru–C2–N1 120.3°/*120.72(13)*°; Ru–C2–N3 135.8/*135.37(13)*°.

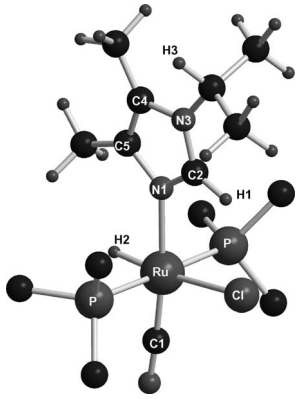


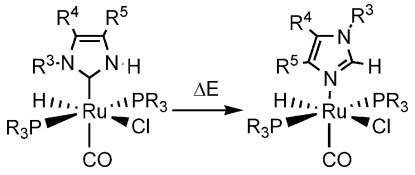
Figure 2. Computed structure of **3** with phenyl groups truncated at the *ipso* carbon atoms. Key distances (Å) and angles (with equivalent experimental data in italics[10]): Ru–N1 2.21/*2.1816(18)*; Ru–C1 1.84/*1.844(3)*; Ru–P(av) 2.39/*2.350(8)*; Ru–Cl 2.60/*2.5453(6)*; Ru–H2 1.59; C2–H1 1.09; H1···Cl 2.42; P–Ru–P 178.4°/*176.89(2)*°; N1–Ru–C1 173.1°/*172.14(9)*°; Ru–N1–C2 122.6°/*124.37(15)*°; Ru–N1–C5 130.6°/*129.75(15)*°.

Most relevant in the context of the present study is the fact that **3** is computed to be 5.6 kcal/mol more stable than **2**, indicating that the *N*-bound species is more stable. This is consistent with the experimental observation that heating **2** at 70 °C in THF in the presence of a base leads to complete conversion to **3**.

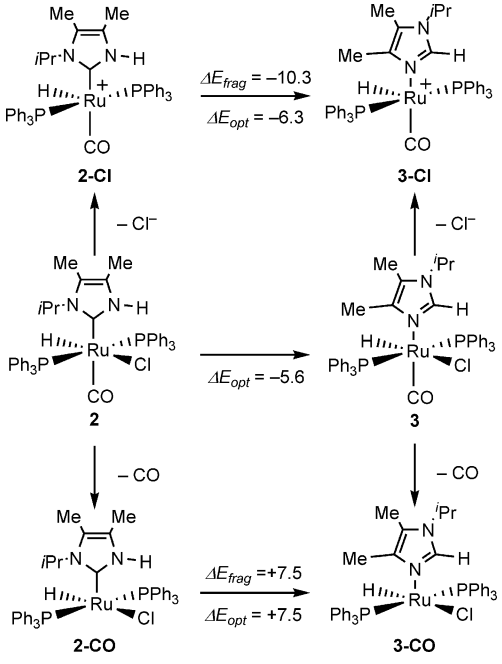
The Role of the *cis*-Cl and *trans*-CO Ligands

In order to delineate the factors behind the greater stability of the *N*-bound tautomer, a series of calculations on model species have been undertaken. Initially the roles played by the ligands *cis* and *trans* to the C2/N1 binding site

are assessed. A second series of calculations then considers systematic variation of the ligand substituents at the N3, C4 and C5 positions (R^3, R^4 and R^5 respectively, see below) and the nature of the phosphane ligand, PR_3 (R = Ph, H). For each model the energy difference, ΔE, between the *N*-bound and *C*-bound tautomers is computed, with a negative value indicating that the *N*-bound form is more stable.



Two conflicting factors that feed into the energetic balance between **2** and **3** are the presence of (i) a *trans*-CO ligand which, having a high *trans* influence, should favour the *N*-bound form, and (ii) a *cis*-Cl ligand that should favour the *C*-bound form through N1–H1···Cl H-bonding.[13] To assess the contribution of each of these components we removed each ligands individually from **2** and **3** and recomputed ΔE for the resultant five-coordinate fragments, initially without allowing for any geometric relaxation. The results are presented as ΔE_{frag} in Scheme 1.



Scheme 1. Computed ΔE [kcal/mol] for **2** and **3** and the five-coordinate species formed upon removal of the *trans*-CO and *cis*-Cl ligands. ΔE_{frag} is the difference between unrelaxed five-coordinate fragments; ΔE_{opt} the difference between fully optimised five-coordinate species. See text for details.

Removal of the *cis*-Cl ligand from **2** and **3** causes ΔE_{frag} to decrease by 4.7 to –10.3 kcal/mol. This compares with ΔE_{opt} = –5.6 for the original compounds, indicating a relative stabilisation of the *N*-bound form, **3-Cl**, over *C*-bound **2-Cl**. This suggests that N1–H1···Cl H-bonding in *C*-bound **2** contributes approximately 5 kcal/mol to the stability of that tautomer. In contrast, removing the *trans*-CO ligand from **2** and **3** causes a complete reversal of stability, with the *C*-bound form, **2-CO**, being 7.5 kcal/mol more stable than *N*-bound **3-CO**. Thus, the presence of a *trans*-CO ligand in **2** and **3** contributes approximately 13 kcal/mol to the greater relative stability of the *N*-bound tautomer. The impact of the *trans*-CO ligand in promoting the greater stability of the *N*-bound tautomer therefore more than counteracts the effect of the *cis*-Cl ligand that tends to favour the *C*-bound form.

In a subsequent step, the structures of the five-coordinate species **2/3-Cl** and **2/3-CO** were allowed to relax to their lowest energy forms. In doing so, we also considered different orientations of the carbene and imidazole ligands. This was particularly important for **2-Cl** as the structure with the *i*Pr group over the vacant metal coordination site is greatly favoured. This is presumably due in part to steric reasons, but this orientation also allows an agostic interaction to develop between the Ru centre and a C–H bond of an isopropyl Me group (see Figure 3). In **3-Cl**, a similar orientation is preferred by the imidazole ligand, where the C5 Me substituent lies over the vacant site. In this case, however, the energetic benefit is less significant, due to the smaller size of the Me group and the lack of a significant agostic interaction with the metal centre. Overall, these considerations favour the *C*-bound form, **2-Cl**, over *N*-bound **3-Cl** and mean that the difference in energy between the optimised five-coordinate species (ΔE_{opt} in Scheme 1) is reduced from –10.3 kcal/mol for the unoptimised fragments to –6.3 kcal/mol.

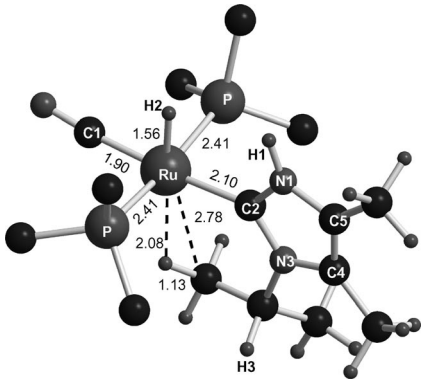
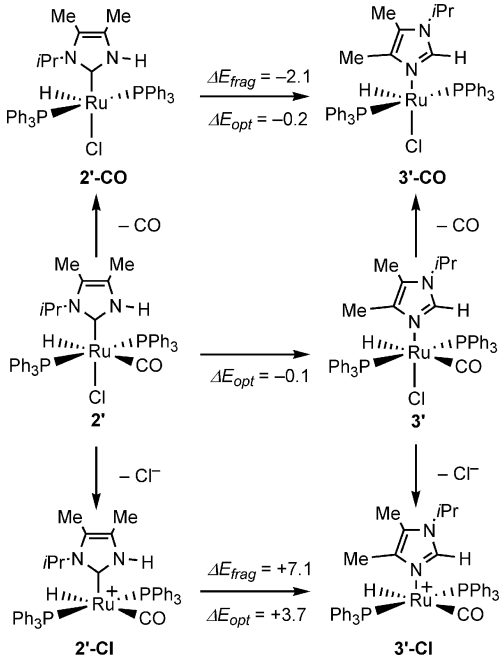


Figure 3. Computed structure of **2-Cl**. Phenyl groups are truncated at the *ipso* carbon and key distances [Å] are indicated.

In five-coordinate **2-CO** and **3-CO** the NHC/imidazole ligands retain the same orientations seen in six-coordinate **2** and **3**. In this case optimisation might be expected to further stabilize the *C*-bound form, however distortion of one PPh_3 ligand in **3-CO** conferred extra stabilisation on this species through a η^2-interaction with one of the phenyl groups (see Supporting Information for full details).[20] As a result ΔE_{opt} remains unchanged from ΔE_{frag} at +7.5 kcal/mol.

The conflicting effects of the Cl and CO ligands can also be seen if these ligands swap position to give the alternative isomers **2′** and **3′**. These species have effectively the same energy (ΔE = –0.1, see Scheme 2)[19] implying a relative sta-

bilisation of the *C*-bound form compared to the **2/3** pair. The dominant factor again seems to be the nature of the *trans* ligand with the stabilising effect of having the weaker *trans* influence Cl ligand *trans* to the carbene in **2′** more than compensating for the loss of N1–H1···Cl H-bonding that was present in **2**.



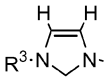
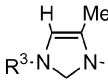
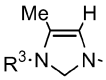
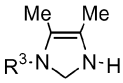
Scheme 2. Computed Δ*E* [kcal/mol] for **2′** and **3′** and the five-coordinate species formed upon removal of the *trans*-Cl and *cis*-CO. See Scheme 1 for the definitions of ΔE_{frag} and ΔE_{opt}.

The effect of ligand removal from **2′** and **3′** is somewhat less pronounced than the equivalent processes from **2** and **3**. Thus loss of the *cis*-CO ligand without geometry relaxation stabilizes the *N*-bound **3′-CO** over **2′-CO** (ΔE_{frag} = –2.1 kcal/mol). **2′-CO** is then relatively stabilised upon optimisation due to the same steric effects and a similar agostic interaction mentioned above for **2-Cl**. Despite this *N*-bound **3′-CO** remains marginally more stable (ΔE_{opt} = –0.2 kcal/mol). The effect of losing the *trans*-Cl ligand to form **2′/3′-Cl** is again complicated by a η^2-interaction between Ru and one PPh_3 phenyl substituent in **3′-Cl**. This preferentially stabilises this species but in this case the *C*-bound form, **2′-Cl**, remains more stable (ΔE_{opt} = +3.7 kcal/mol). Overall, it is noteworthy that for both the **2/3** and **2′/3′** pairs loss of a ligand *trans* to the C2/N1 binding site leads to square-pyramidal species that are more stable as the *C*-bound tautomers.

The Role of the Heterocyclic Ligand Substituent Groups

The effects of varying the ligand substituents, R^3, R^4 and R^5, around the ring are now considered. Calculations were performed with {Ru(Cl)(H)(CO)(PR_3)$_2$} fragments, with either PPh_3 or PH_3 ligands in place. An initial comparison where **2** and **3** were recomputed with PH_3 ligands gave a value for Δ*E* of –4.8 kcal/mol, very similar to the value of –5.6 kcal/mol seen for the full models. The effect of the PPh_3 ligand is therefore relatively minor. As a result the calculations varying the ligand substituents focussed on the smaller {Ru(Cl)(H)(CO)(PH_3)$_2$} fragment (see Table 1). Selected calculations were repeated with the PPh_3 ligands, but as found above, these had a minor effect, stabilizing the *N*-bound form by ca. 1 kcal/mol in each case (data in parenthesis, Table 1).

Table 1. Computed Δ*E* [kcal/mol] between the *C*- and *N*-bound forms of 3-R-imidazol-2-ylidenes at {Ru(Cl)(H)(CO)L_2} fragments (L = PH_3 or PPh_3).[a]

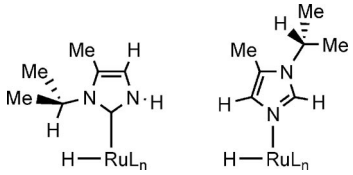
R^3	 **1**	 **2**	 **3**	 **4**
H	–2.2 (–3.0)	–0.7 (–1.4)	–1.8 (–2.7)	–0.6 (–0.9)
Me	–3.7 (–4.6)	–2.3 (–3.5)	–3.6 (–4.5)	–2.0 (–3.8)
Et	–4.0	–2.4	–4.4	–2.5
*i*Pr	–4.1 (–5.2)	–2.6 (–3.5)	–6.3 (–7.1)	–4.8 (–5.6)
*t*Bu	–9.4	–7.9	–13.6	–12.5

[a] Numbers in parenthesis are where L = PPh_3.

During the discussion of the full experimental structures, a pronounced tilting of the NHC in **2** and (to a lesser extent) the imidazole in **3** toward the *cis*-Cl ligand was noted. This tilting is retained in the structure of the *C*-bound form computed with the simplest model (i.e. $R^3/R^4/R^5$ = H; L = PH_3), albeit somewhat reduced (Ru–C2–N1 = 124.1°, Ru–C2–N3 = 132. 1°, H1···Cl = 2.22 Å; cf. 120.3°, 135.8° and 2.19 Å in **2**). The tilting distortion therefore appears to be driven primarily by the stabilising N1–H1···Cl interaction, amplified in the full system by the steric bulk of the *i*Pr group at N3. For the small model of **3** the degree of tilting is again reduced compared to the full system (Ru–N1–C2 = 125.2°, Ru–N1–C5 = 127.8°, H1···Cl = 2.48 Å, cf. 122.6°, 130.6° and 2.42 Å in **3**). The tilt in the small model could be considered insignificant, however, computation of an alternative structure where the imidazole ligand was rotated by 180° such that the C5–H bond is directed towards Cl resulted in a destabilization of 2 kcal/mol. Thus, the interaction of the more acidic C2–H1 bond with the *cis*-Cl ligand is not negligible and could also contribute to the energetic balance between *C*- and *N*-bound tautomers. For this reason all *N*-bound structures in Table 1 were computed with the C2–H1 bond oriented toward Cl.

Turning to the data in Table 1, the first column gives Δ*E* values for simple ligands where R^4 = R^5 = H and shows that the *N*-bound tautomer becomes more favoured as the size of the substituent at N3 increases. This is particularly apparent for R^3 = *t*Bu with Δ*E* more than doubling (–9.4 kcal/mol) compared to the result when R^3 = *i*Pr (–4.1 kcal/mol). The reason for this can be traced to the structure of **2** shown in Figure 1. In **2** the methine C–H3 bond of the *i*Pr group can be directed towards H2; however when R^3 = *t*Bu this position is now occupied by a Me group and this has a significant steric impact that destabilises the *C*-bound form.

The remaining columns in Table 1 monitor the effects of Me substituents at the C4 and C5 positions, introduced first individually, and then in combination. In each series greater steric bulk at N3 again increasingly favours the *N*-bound tautomer. For a given substituent at N3, introducing a Me substituent at C5 causes a relative destabilization of the *N*-bound tautomer by about 1.5 kcal/mol (compare columns 1 and 2). This destabilization of the *N*-bound form arises from having the bulkier (compared to R^5 = H) Me group over the Ru–H2 bond (cf. the structure of **3** in Figure 2). Substitution at C4 is more subtle (column 3). For smaller N3 substituents (R^3 = H, Me) the *N*-bound tautomer becomes relatively less stable. However, when R^3 = *i*Pr or *t*Bu the relative stability of the *N*-bound form is increased, by 2.2 kcal/mol and 4.2 kcal/mol, respectively (column 1 vs. column 3). This appears to arise from the restricted movement of these bulky N3 substituents in the *C*-bound form. For an *i*Pr substituent the favoured orientation has the methine C–H3 pointing toward H2 and lying parallel to the Ru–C2 bond. This has the consequence of placing the isopropyl Me groups close to the C4 Me (see Scheme 3). In the *N*-bound tautomers the *i*Pr group can rotate such that its methine C–H2 bond is directed towards the neighbouring Me group on C4. The enhanced steric encumbrance associated with a C4 substituent is therefore much more significant in the *C*-bound tautomer. The situation is further exacerbated when R^3 = *t*Bu.



Scheme 3. Introducing a Me substituent at the C4 position results in enhanced steric interactions in the *C*-bound tautomer.

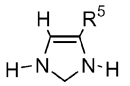
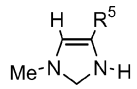
The effect of having Me substituents at both C4 and C5 appears to be approximately additive (column 4). Thus for small N3 substituents, having Me groups at both C4 and C5 destabilises the *N*-bound form, while for larger substituents at N3 the impact of the groups at C4 and C5 counteract each other. Overall, none of the systems considered in Table 1 provides an example where the *C*-bound form is predicted to be the more stable. The closest example is when R^3 = H and R^4/R^5 = Me for which ΔE = –0.6 kcal/mol.

NHC Ligands That Stabilise the C-Bound Tautomer

In a final series of calculations we considered which combination of ring substituents might lead to the *C*-bound tautomer of an NHC ligand being more stable than the *N*-bound alternative. These calculations are based on the {Ru(Cl)(H)(CO)(PPh_3)$_2$} fragment employed in the experimental system. The results in the preceding section suggest that *C*-bound tautomers are favoured with a large group at C5 in combination with small groups at N3 and, preferably, C4. We therefore computed ΔE for two series of ligands where R^3 = R^4 = H and R^3 = Me, R^4 = H. In each case the R^5 substituent is then varied.

The results in Table 2 indicate that for R^3 = H increasing the size of the R^5 substituent to an *i*Pr group is required to favour the *C*-bound form, although as ΔE = +0.3 kcal/mol this preference is clearly still marginal. Going to R^5 = *t*Bu produces a significant preference for the *C*-bound form (ΔE = +6.6 kcal/mol) and a Ph substituent at C5 also favours the *C*-bound form by 2.8 kcal/mol. Similar trends are computed in the second series where R^3 = Me. As this larger substituent at N3 tend to stabilise the *N*-bound tautomer only the ligands where R^5 = *t*Bu and Ph are predicted to be more stable in their *C*-bound tautomers when bound to {Ru(Cl)(H)(CO)(PPh_3)$_2$}.

Table 2. Computed energy differences [kcal/mol] between the *C*- and *N*-bound tautomers of 5-R-imidazol-2-ylidenes and 3-Me-5-R-imidazol-2-ylidenes at the {Ru(Cl)(H)(CO)(PPh_3)$_2$} fragment.

R^5	 **1**	 **2**
H	–3.0	–4.6
Me	–1.4	–3.5
*i*Pr	+0.3	–1.6
*t*Bu	+6.6	+4.1
Ph	+2.8	+1.1

Conclusions

Density functional calculations have been employed to delineate the factors that control the energetic preference for the *C*- and *N*-bound tautomers of [Ru(Cl)(H)(CO)(PPh_3)$_2$(I*i*PrMe$_2$)] (I*i*PrMe$_2$ = 3-isopropyl-4,5-dimethylimidazol-2-ylidene), **2** and **3**, respectively. The location of the high *trans* influence CO ligand *trans* to the C/N binding site is the dominant factor that makes the *N*-bound tautomer more stable. This preference is reinforced by the bulky *i*Pr substituent at N3. Calculations predict that analogous species with 5-R-imidazol-2-ylidene or 3-Me-5-R-imidazol-2-ylidene (R = *t*Bu or Ph) would be more stable as the *C*-bound tautomer. In addition, the *C*-bound tautomers become much more accessible in five-coordinate square pyramidal species derived from **2** or **3**, and indeed become the more stable form when the NHC ligand is located *trans* to the vacant site.

Experimental Section

All density functional theory calculations were run with Gaussian 03[21] using the BP86 functional.[22] Ru, P and Cl centres were described with the Stuttgart RECPs and associated basis sets[23] with a set of d-orbital polarisation functions on P (ζ = 0.387) and Cl (ζ = 0.640).[24] 6-31G** basis sets were used for all other atoms.[25] All stationary points were fully characterized by analytical frequency

calculations as minima (all positive eigenvalues). Reported energies include a correction for zero-point energies. Test calculations using a range of different functional and basis set combinations indicated that the computed difference in energy between **2** and **3** was insensitive to the method employed (see Supporting Information).

Supporting Information (see also the footnote on the first page of this article): All computed structures and energies.

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