π-Face donor properties of N-heterocyclic carbenes†

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The donor properties of aryl substituted N-heterocyclic carbenes are characterized by lone pair donation from the carbene carbon *and*, as is shown here, by donation of electron density of the aromatic π-face of the NHC aryl groups towards the metal.

N-Heterocyclic carbenes (NHC) turn out to be a increasingly important class of ligands, which has found numerous applications in homogeneous catalysis;[1] especially in various cross coupling reactions (Heck, Sonogashira, Suzuki–Miyaura, Buchwald–Hartwig amination),[2–6] hydrosilylation[7] and in the Ru-mediated olefin metathesis.[8,9] For the latter reactions utilizing Ru-based Grubbs II[10] and Grubbs–Hoveyda type catalysts,[11] NHC ligands have demonstrated their superiority to the more traditional phosphines, owing to their special donor properties.[12] Consequently, it is highly desirable to better understand the precise nature of NHC as a ligand. The importance of precisely controlling electronic and steric properties of olefin metathesis catalysts was demonstrated recently by Grela and co-workers, who systematically modified the 2-isoproxybenzylidene fragment in olefin metathesis catalysts of the Grubbs–Hoveyda type, to generate significantly more active catalysts.[13,14]

Various attempts have been made to quantify the electronic properties of NHC ligands, notable in this respect is work from Nolan and co-workers.[15–17] Typically the *ν*(CO) of selected NHC metal carbonyls is monitored,[17,18] to indirectly study the electron density transferred from the NHC ligand *via* the metal. Probing the Ru(II)/Ru(III) redox potential by cyclic voltammetry should also be a useful tool to gain information on the electronic situation at the metal center. Consequently, we have synthesized a number of Grubbs II and Grubbs–Hoveyda type complexes with modified NHC ligands and have determined their redox potentials.

The synthesis of the various Grubbs–Hoveyda type catalysts follows the general scheme outlined in Fig. 1; omitting the reduction of the diimine, leads to the corresponding ruthenium complexes with unsaturated NHC ligands. However, while the various complexes $Cl_2Ru(CHC_6H_4O\textit{i}Pr)(SIXylR)$ with saturated ligands are highly stable green powders, the related unsaturated complexes $Cl_2Ru(CHC_6H_4O\textit{i}Pr)(IXylR)$ form brownish-green materials, which slowly decompose during chromatography and display only limited stability in solution. Surprisingly the imidazolium based Grubbs–Hoveyda complexes are virtually unknown in the literature and we are only aware of work from Buchmeiser, Nuyken and co-workers who describe catalytic tests with complex **11**, which turned out to be inactive in the cyclopolymerization of 1,6-heptadyines.[19]

The redox potentials of various Ru(II)/(III) complexes determined by cyclic voltammetry are presented in Table 1. The Ru electrochemistry is close to reversible up to scan rates of 2000 mV s^{-1} as evidenced by the small differences of the anodic and cathodic peak potential of between 60 and 91 mV. At least on this time scale there is no evidence for EC-processes. The redox potentials within the two pairs of Grubbs II complexes $(Cl_2Ru(CHPh)(IXylR)(PCy_3)$ **2**/$Cl_2Ru(CHPh)(SIXylR)(PCy_3)$ **3** and $Cl_2Ru(CHPh)(IXylR)(PCy_3)$ **4**/$Cl_2Ru(CHPh)(SIXylR)(PCy_3)$

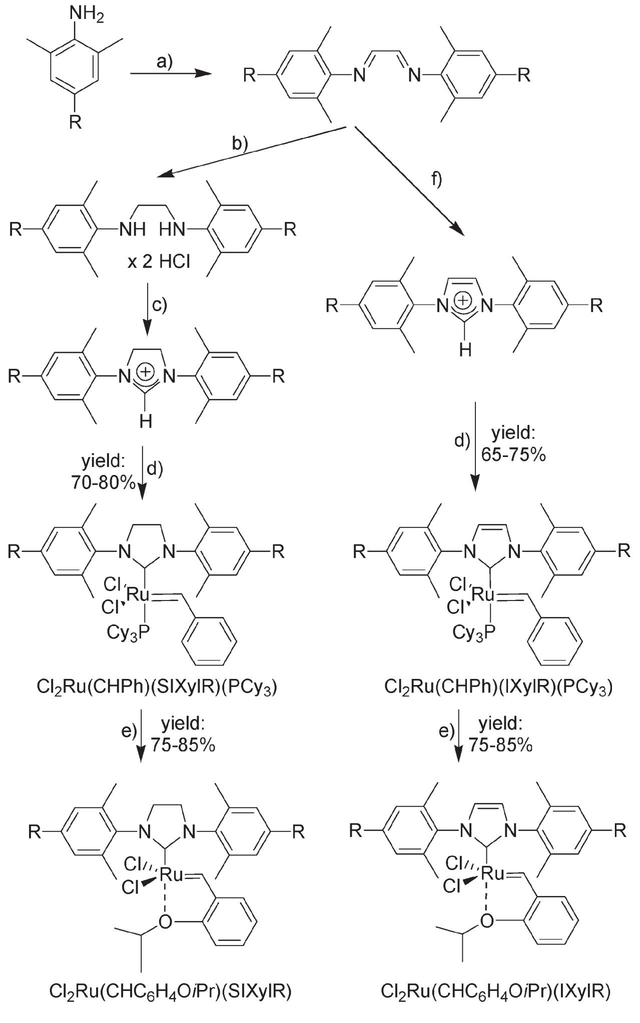

Fig. 1 Synthesis of substituted Grubbs II and Grubbs–Hoveyda type complexes. *Reagents*: (a) glyoxal, HCOOH; (b) $LiAlH_4$, thf; (c) $HC(OEt)_3$, HCOOH; (d) KO*t*Bu, Grubbs I, toluene–thf; (e) CuCl, 2-isopropoxystyrene; (f) HCHO, HCl, dioxane.

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Table 1 Redox potentials of ruthenium complexes studied by cyclic voltammetry (scan rate 100 mV s^{-1} in CH_2Cl_2, 0.1 M $TBAPF_6$.

Compound		R	$\Delta E_{1/2}$/V	$(E_a - E_c)$/mV
$Cl_2Ru(CHPh)(PCy_3)_2$	**1**	—	0.585	87
$Cl_2Ru(CHPh)(IXylR)(PCy_3)$	**2**	Me	0.455	82
$Cl_2Ru(CHPh)(SIXylR)(PCy_3)$	**3**	Me	0.447	77
$Cl_2Ru(CHPh)(IXylR)(PCy_3)$	**4**	Br	0.536	75
$Cl_2Ru(CHPh)(SIXylR)(PCy_3)$	**5**	Br	0.537	74
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIXylR)$	**6**	H	0.870	90
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIPr)$	**7**	H	0.895	76
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIXylR)$	**8**	$OC_{12}H_{25}$	0.836	87
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(IXylR)$	**9**	$OC_{12}H_{25}$	0.756	84
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIXylR)$	**10**	Me	0.850	91
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(IXylR)$	**11**	Me	0.765	75
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIXylR)$	**12**	Br, H	0.905	82
$Cl_2Ru(CHC_6H_4O\mathit{i}Pr)(SIXylR)$	**13**	Br	0.935	74

5 are almost identical, while the two bromine substituted complexes **4** and **5** are anodically shifted by *ca.* +85 mV with respect to **2** and **3**. Obviously, but somewhat unexpectedly the variation of the R group in the periphery of the complex has a profound influence on the redox potential Ru(II)/(III).

The change from a Grubbs II to a Grubbs–Hoveyda catalyst and consequently the presence of an ether oxygen donor instead of PCy_3 trans to the NHC, results in a drastic anodic shift of the redox potential of +400 mV (**5**→**13**). Next, the influence of the remote groups R on the Ru(II)/Ru(III) redox potential in the Grubbs–Hoveyda complexes was studied in a more systematic manner. Again we were surprised to observe significant shifts of the redox potentials, as a function of the nature of the R group (Table 1, Fig. 2), which are in accord with the electron donating ability of the remote substituents. This is obvious when comparing the series of **6**, **8**, **10**, **12** and **13** (Fig. 2). It is also worth noting that the *para*-substituents also have an effect on the stability of the respective ruthenium complexes. In this vein, the more electron donating substituents, especially –OR, lead to a significant destabilisation of the respective Grubbs II and Grubbs–Hoveyda complexes as evidenced by some decomposition during chromatographic purification.

At least three questions arise from the results of the experimental studies presented above.

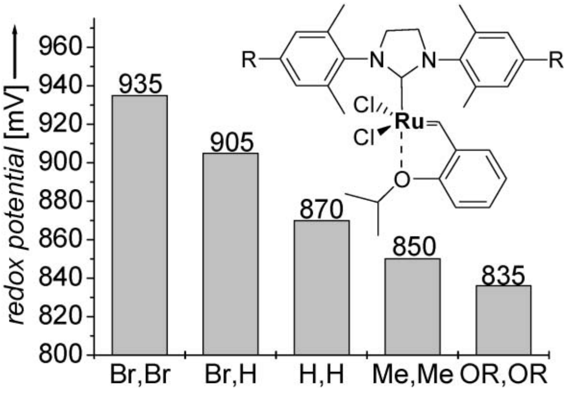

Fig. 2 Redox-potentials of Grubbs–Hoveyda type catalyst complexes with variable R group.

(a) Why have substituents on the phenyl ring in the position *para* to the nitrogen atom such a profound influence on the redox potential of the remote ruthenium center?

A quick answer would be to assume the transfer of electronic information from the *para*-substituents across the system of conjugated double bonds to the ruthenium center. However, on closer inspection of the complexes, one immediately realizes that this can hardly be the case. First of all, the shortest bond path between the ruthenium metal and the *para*-substituents entails seven covalent bonds, furthermore, the planes of the six-membered ring and that of the five-membered ring are orthogonal. Given these restraints a through bond mechanism appears to be extremely unlikely. In order to come up with an explanation for the remote substituents effect it is useful to analyze the X-ray crystal structures of a Grubbs II,[10] a Grubbs–Hoveyda type catalyst,[20] and a related NHC–Ru complex.[21] In these structures the planes of the arene rings are almost coplanar with the plane formed by $Cl_2Ru{=}C$ unit. However, for the Grubbs II complex the Ru=CH unit is in the same plane resulting in a face-to-face orientation of the respective π-orbitals, while in the Grubbs–Hoveyda catalyst the respective C–H unit is pointing towards the center of the six-membered ring, resulting in an even more intimate contact of the two units. Common to both structures are the rather short distances of two planes, which for the phenyl carbon bonded to nitrogen (*i.e.* in the *para*-position to the variable group R) and the benzylidene carbon are close to 305 pm. Consequently, we believe that the transfer of the electronic information from the aromatic ring into the transition metal center occurs through this pathway.

(b) Why is there such a significant difference in the redox potentials of the saturated and the unsaturated N-heterocyclic carbene ruthenium complexes of the Grubbs–Hoveyda type.

Several studies in the literature have been devoted to studying the donor properties of saturated and unsaturated NHC versus phosphine ligands. As indicated above there can be no doubt that NHC ligands are significantly more electron-donating than phosphines. This is confirmed on comparing the Ru(II)/(III) redox potentials of **1** (+0.585 V), **2** (+0.455 V) and **3** (+0.448 V). Replacing a single phosphine ligand (PCy_3) by a NHC ligand results in a cathodic shift of the redox potential by *ca.* 130 mV, while the redox potentials of **2** and **3** are almost identical. This situation changes drastically in the Grubbs–Hoveyda type complexes. Here the Ru(II)/(III) redox potentials of complexes with saturated NHCs are significantly more anodic (by 75–100 mV), than those with the unsaturated NHC ligands. Based on these results alone, it is tempting to propose that the unsaturated NHC ligands are better donors than their saturated counterparts. However, obviously the similarity of the redox potentials of **2** and **3** and of **4** and **5** does not support this view. It might be of significance in this respect, that in the Grubbs II type complexes a strong σ-donor (PCy_3) in the trans position is replaced by a weak ether donor (ether oxygen) in the Grubbs–Hoveyda catalysts. Since on the other hand the differences in the redox potential are of the same order as those induced by the various *para*-substituents, it can not be excluded that subtle structural differences between the Grubbs–Hoveyda complexes with saturated and unsaturated ligands account for the different redox potentials. It should, however, be noted here that very recently Nolan and co-workers,[17] based on an analysis of the IR spectra of

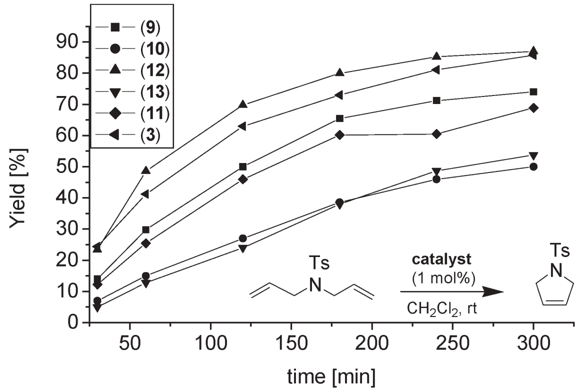

Fig. 3 Product formation in the RCM with electronically modified catalysts.

complexes of the $(NHC)Ni(CO)_3$ type, stated that, contrary to the common assumption, unsaturated NHC ligands might be better donors than their saturated relatives.

(c) Do these differences in the electronic situation at the ruthenium center translate into modified catalytic properties?

We have performed preliminary tests of the various Grubbs–Hoveyda type catalysts described here in the ring closure metathesis of diallyltosylamine. It is obvious from the data presented in Fig. 3, that the variable electronic situations at the different ruthenium centers has a profound influence on the catalytic activity, which depending on the nature of the R changes by up to 500%. On the other hand, for the present set of data we could not observe a correlation between the redox potential Ru(II)/(III) and the catalytic activity.

In conclusion, the variation of the remote substituents R on the phenyl ring of N-heterocyclic carbenes has a significant influence on the redox behavior of olefin metathesis catalysts of the Grubbs II and the Grubbs–Hoveyda type and can be used to modify the catalytic activity of such complexes. Obviously, the electronic properties of NHC ligands are not exclusively governed by the σ-donation from the carbene carbon atom; transfer of electron density between the Ru=CHR unit and the phenyl rings also has to be taken into account.

As evidenced by cyclic voltammetry studies of Grubbs–Hoveyda type complexes, the saturated and the unsaturated NHC ligands can give rise to significantly different redox potentials Ru(II)/(III). The systematic changes of the redox potential according to the electron donating nature of the remote substituents and the fact that the aryl ring is electronically decoupled from the nitrogen heterocycles provides strong evidence of the π-face coordination of the Ru–carbene. It will be the subject of extensive future studies to elucidate the effect of the remote substituents on the catalytic activity and to understand whether unsaturated NHC ligands posses an intrinsically superior donor ability or if other effects, unique to the Grubbs–Hoveyda catalyst, are responsible for the unexpected redox potential shifts.

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