

Fig. 7 ^1H - ^1H NOESY spectra showing dependence of Ru-NHC rotation on NHC unsaturation. (a) Exchange correlations between mesityl methyl signals for the IMes derivatives. (b) Absence of correlations for the H_2IMes analogues. (all in C_6D_6 , 500.1 MHz, 25 $^\circ\text{C}$, 1.5 s relaxation delay). Symbols: (\wedge) = Cy; for others, see top.

this possibility for **s-GIIIm**. It was rejected, as calculations at the level of theory then available indicated limited $\text{Ru} \rightarrow \text{PCy}_3$ backbonding (in consequence of which, stronger PCy_3 binding was attributed to an enhanced Ru/PCy_3 electrostatic attraction). Importantly, however, consideration of dispersion forces has since emerged as critical to quantitative evaluation of the PCy_3 dissociation step.⁴⁰

The limited role heretofore assigned to $\text{Ru}-\text{PCy}_3$ π -acceptor interactions in this system is perhaps unsurprising, given the widespread perception of alkylphosphines as strong σ -donors and weak π -acceptors (a situation also encountered in the context of NHC donicity; see above). Here too, however, a re-evaluation is in progress. In an analysis of electron density and structural effects, Leyssens, Harvey and co-workers demonstrated that π -backbonding from the metal atom onto the $\text{P}-\text{R}$ σ^* -antibonding orbitals can represent a significant component of metal-phosphine bonding, including for tri-alkylphosphine complexes.⁴¹ A recent leading review of computational approaches to the understanding of metal-phosphorus bonding likewise emphasizes that calculated ligand descriptors for phosphine ligands must consider their π -acceptor character.⁴²

In light of these developments, we suggest that π -back-donation onto the phosphine is a significant, overlooked contribution to the low PCy_3 lability in the second-generation Grubbs catalysts. The potent σ -donor properties of the NHC ligand constrain back-donation onto any π -acceptor ligands present. For precatalyst **s-GII**, three ligands can participate in π -backbonding: H_2IMes , PCy_3 , and benzylidene.³⁹ In the case of **u-GIIIm**, the poor π -acceptor character of the IMes and methylidene ligands leaves the PCy_3 ligand as the sole entity that can ameliorate the buildup of charge on the metal. We propose that this buildup is offset for **u-GIIIm** by greater $\text{Ru} \rightarrow \text{PCy}_3$ back-donation (Fig. 8), and for **s-GIIIm**, by greater $\text{Ru} \rightarrow \text{H}_2\text{IMes}$ back-donation, accompanied by a lesser amount of $\text{Ru} \rightarrow \text{PCy}_3$ back-donation. This would account for the poor net charge donation from the saturated NHC ligand observed in the Kennepohl study. Also relevant in this context is an energy decomposition analysis by Poblet and co-workers, which suggested that the π -acceptor capacity of H_2IMes reduces total charge donation to the metal for **s-GIIIm**, relative to its IMes analogue.²¹

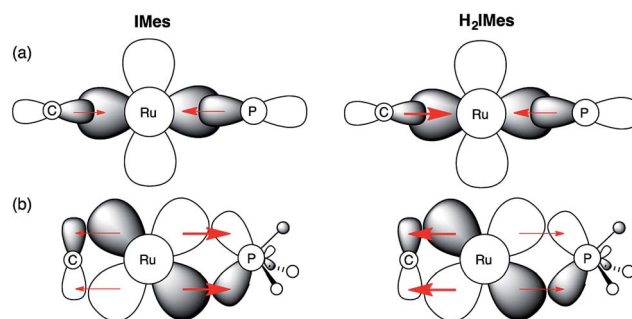


Fig. 8 Impact of NHC π -acidity on PCy_3 lability. (a) σ -Bonding interactions; (b) π -bonding interactions. Perspective down the $\text{Ru}=\text{CHR}$ bond.



- 40 See: ref. 22, 34 and background discussion in: Y. Zhao and D. G. Truhlar, *Org. Lett.*, 2007, **9**, 1967–1970.
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- 45 For further improvements in synthesis of **GIm**, see: J. A. M. Lummiss, A. G. G. Botti and D. E. Fogg, *Catal. Sci. Technol.*, 2014, **4**, 4210–4218.

