

Poster Presentation

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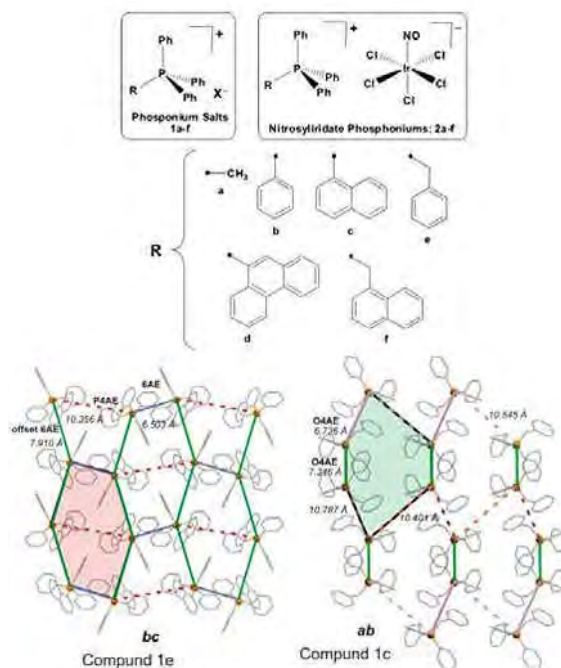
A new family of $[\text{IrCl}_5(\text{NO})]^-$ salts. Structural diversity tuned by aryl embraces

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The interactions experimented by multiple phenyl or other aromatic groups in crystals have been described as “embraces” since 1995, when Dance and co-workers developed the embrace paradigm as an important and widespread tool of supramolecular chemistry. There are three main classes of Multiple Phenyl Embraces (MPE) depending on the total number of phenyl rings (Ph) located in the interaction domain: sextuple (6PE), quadruple (4PE), and double phenyl embrace (2PE) [1]. Recently, an accurate theoretical evaluation of the MPE motifs between PPh_4^+ was presented by Novoa et al [2]. In our laboratory we demonstrated that by changing the counterion of the $[\text{IrCl}_5(\text{NO})]^-$ salts from K^+ to PPh_4^+ , it was possible to stabilize an excited state of the metal complex anion. The electronic distribution of the IrNO moiety in $\text{K}[\text{IrCl}_5(\text{NO})]$ can be depicted as the closed-shell electronic structure $\text{Ir}^{\text{III}}-\text{NO}^+$. However, in $\text{PPh}_4[\text{IrCl}_5(\text{NO})]$ an unprecedented electronic perturbation takes place favouring the open-shell electronic structure $\text{Ir}^{\text{IV}}-\text{NO}^*$ [3]. These results together with the interesting systematic studies on MPE, encouraged us to explore the synthesis of new phosphonium salts. In this work we report new phosphonium ions of the type Ph_3PR^+ and five new $\text{Ph}_3\text{PR}[\text{IrCl}_5(\text{NO})]$ salts (R = aryl, methylaryl). Structural analyses of these compounds were done in the context of the multiple embraces motifs. For the new unsymmetrical $[\text{IrCl}_5(\text{NO})]^-$ salts, the supramolecular arrangements are different from the one observed for the PPh_4^+ one. In the last one, the 4PE infinite chains run parallel to the columns described by the anions [3] and for the others, the presence of bulkier substituents give place to symmetries that favours other kinds of aryl embraces resulting in a side by side location of the anions. Finally, DFT calculations were performed to evaluate the theoretical concerns regarding the structural behaviour, as well as the electronic distribution along the family of compounds.

[1] I. Dance, M. Scudder. *CrystEngComm*, 2009, 11, 2233-2247 and references therein., [2] E. D’Oria, D. Braga, J Novoa. *CrystEngComm*, 2012, 14, 792-798., [3] F. Di Salvo, N. Escola, D. Scherlis, et al. *Chem. Eur. J.* 2007, 13, 8428-8436.



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