Everything new is the well-forgotten old. The 1,3,5-triazapentadiene case

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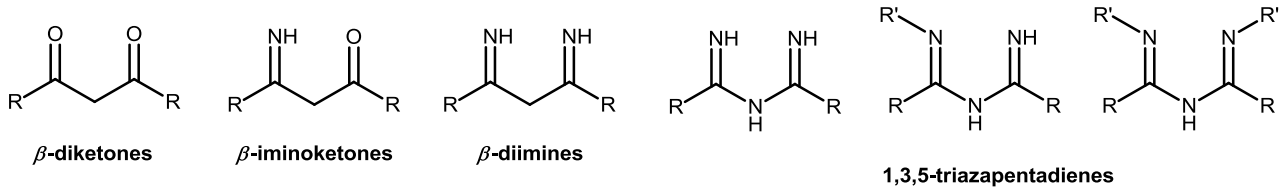
Despite their discovery more than a hundred years ago, the chemistry of 1,3,5-triazapentadienes (TAP), which comprise the class of nitrogen analogues of β-diketones, is much less developed as compared to the related oxygen-containing species. Unlike the other *N*-derivatives of β-diketones, such as β-iminoketones and β-diimines, TAPs bear one additional donor site at the central N atom, and recent DFT calculations indicated that these species possess an even greater potential for sequestering various metal centers (e.g., Cu^{II}, Zn^{II}, and Pd^{II}) than the related β-diketones. Until now, the experimental approaches to TAP metal complexes were poorly developed, in spite of the fact that some members of this family are known to exhibit useful properties.



In the framework of our ongoing project on reactions of metal-activated nitriles and based on our interest in the chemistry of TAP transition metal complexes (see references below), we have elaborated novel general protocols for metal-mediated generation of TAP species. Neutral bis-chelated platinum(II)-TAP complexes were found to exhibit intensive phosphorescent properties. In addition, TAP-based metal complexes support weak interactions of small molecules (e.g., solvents) and allow the identification of unusual hydrogen- and halogen bondings. All these issues will be presented, along with a brief overview of the literature on excising TAP systems and their properties.

Publications from Kukushkin's group on (*i*) metal-mediated generation of TAP complexes: *Inorg. Chem.*, **52** (2013) 6378; **48** (2009) 8678; **48** (2009) 2583; **47** (2008) 3088; **44** (2005) 5152; **42** (2003) 7239; *Dalton Trans.*, 2008, 5220; *Chem. Eur. J.*, **13** (2007) 786; *JACS*, **126** (2004) 15040; (*ii*) phosphorescent properties of (TAP)Pt^{II} systems: *Inorg. Chem.*, **47** (2008) 11487; *Dalton Trans.*, 2006, 3798; (*iii*) weak molecular interactions supported by TAP species: *J. Phys. Chem., A*, **117** (2013) 2827; *Dalton Trans.*, **41** (2012) 6922; *Crystal Growth & Design*, **10** (2010) 4839; *Eur. J. Inorg. Chem.*, 2007, 4621.

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