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# BOOK OF ABSTRACTS

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# Dimeric Mixed Valence and Trimeric Palladium(0) complexes: Recent Updates

A. Dariol[1], F. Ferretti[1], P. Macchi[2], and F. Ragaini[1*]

[1] Dept. of Chemistry, University of Milan, Italy and Consorzio INSTM
[2] Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Italy

* fabio.ragaini@unimi.it

Ar-BIAN (bis(arylimino)acenaphthene) Schiff bases have found wide application as ligands for both transition and main group metals because their rigid structure imparts the correct geometry for chelation and improves the stability of the compounds against hydrolysis and rupture of the central C-C bond. We have previously reported on the synthesis of the reduced form of the BIAN compounds, Ar-BIAN$H_2$ [1]. In a previous conference, we also reported on the use of Ar-BIAN$H_2$ compounds to generate unprecedented trimeric formally Pd(0) complexes only stabilized by Ar-BIAN ligands in which each palladium atom is coordinated in a standard $\kappa^2$N chelating way to an Ar-BIAN ligand and in a $\eta^2$ way to a C=N double bond of another Ar-BIAN ligand. A dimeric Pd(0)-Pd(II) complexes showing the same type of coordination was also mentioned. We have now extended the family of trimeric complexes to mixed Ar,Ar'-BIAN ligands [2], having different substituents on the two aryl rings and to dimeric complexes with different Ar-BIAN ligands (Figure 1, right for one example). Interestingly, in the former case, only one isomer among all possible ones is formed, corresponding to that in which palladium coordinates only to the C=N bonds whose nitrogen bears the more electronwithdrawing substituent (Figure 1, left). Also noteworthy is the fact that the complex has a helical chirality. Several complexes were synthesized and crystallographically characterized and generally, the two enantiomers co-crystallize, but when *m*-Pr$^i$C$_6$H$_4$-BIAN was employed as ligand, enantiomerically pure single crystals of both enantiomers could be obtained and separately analyzed by X-ray diffraction (Figure 1, middle).
The chemistry of the trimers was also preliminary investigated, including ligand substitution, reactions with olefins and oxidative addition reactions.

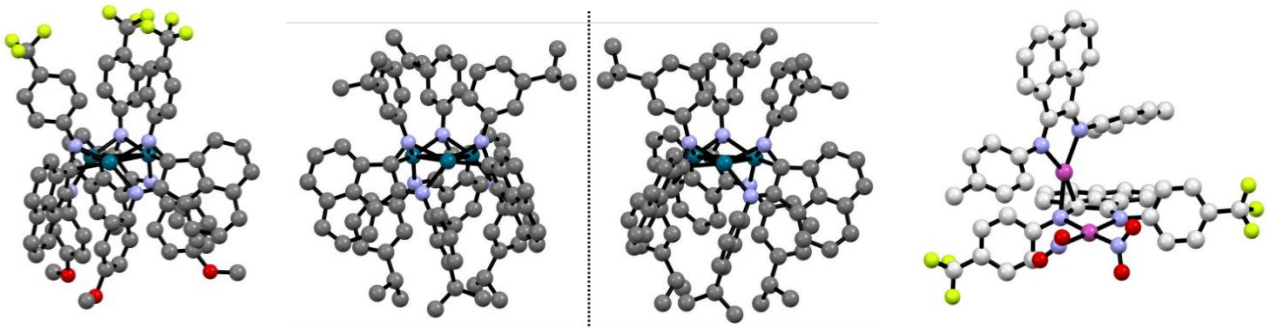

Figure 1. Trimeric and dimeric palladium(Ar-BIAN) complexes.

## References

[1] M. Viganò, F. Ferretti, A. Caselli, F. Ragaini, M. Rossi, P. Mussini, P. Macchi (2014) 'Easy Entry into Reduced Ar-BIAN$H_2$ Compounds: A New Class of Quinone/Hydroquinone-Type Redox-Active Couples with an Easily Tunable Potential', Chem. Eur. J., 20:14451

[2] M. Gasperini, F. Ragaini, E. Gazzola, A. Caselli, P. Macchi (2004) 'Synthesis of mixed Ar,Ar '-BIAN ligands (Ar,Ar '-BIAN = bis(aryl) acenaphthenequinonediimine). Measurement of the coordination strength of hemilabile ligands with respect to their symmetric counterparts', Dalton Trans., 3376–3382.