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Schiff Bases of the BIAN Family: from Symmetrical Biaryl Derivatives to Mixed, Alkyl, Chiral or Reduced Ligands and Heterogeneous Catalysts.

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The number of applications of *bis-imines* as ligands in homogeneous catalysis has much increased in recent years. Derivatives of acenaphthenequinone (R-BIANs) are especially useful to this purpose because the rigidity of the acenaphthene skeleton strengthen coordination to a metal and add stability against the rupture of the central C-C bond of the diimine moiety.

During the years, we have expanded the available range of Ar-BIANs to ligands where the aryl group bears strongly electronwithdrawing substituents (1), two different aryl groups are present (2), and first prepared usually unstable Alkyl-BIAN compounds (3,4). The key principles which allowed these products to be obtained will be illustrated. Solubility of the products and the right control of ring strain for alkyl derivatives are essential points.

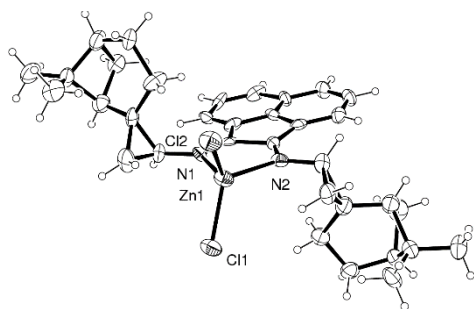
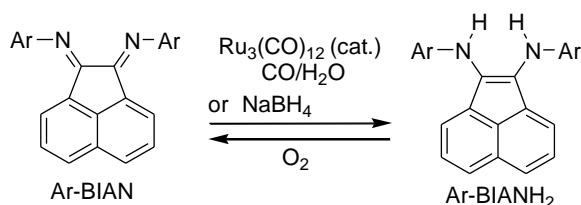


Figure 1

The coordinating strength of a series of Ar-BIAN ligands to several palladium complexes has been measured and varies linearly with the log of Hammett σ constant. The slope of the correlation (ρ) depends on the metal complex and can be regarded as measure of its Lewis acidity (5).

The family of R-BIAN ligands was then further expanded to chiral derivatives (6) (Figure 1) and finally to reduced ligands, Ar-BIANH₂ (7) (Figure 2). The latter are air sensitive compounds, but are stable under in the solid state an inert atmosphere and can be employed to synthesize catalytically active complexes without resorting to the use of reduced metal precursors or alkaline-metal reduced intermediates (8).

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this evolution, the last application decompose the coordinated ligand at temperatures to generate

heterogeneous nitrogen- enriched graphitic cobalt catalysts, effective in hydrogenation reactions for which traditional cobalt catalysts are inactive (9).

Figure 2

References:

1. M. Gasperini, F. Ragaini, S. Cenini *Organometallics*, **2002**, *21*, 2950.
2. M. Gasperini, F. Ragaini, E. Gazzola, A. Caselli, P. Macchi *Dalton Trans.*, **2004**, 3376.
3. F. Ragaini, M. Gasperini, E. Gallo, P. Macchi *Chem. Commun.*, **2005**, 1031.
4. F. Ragaini, M. Gasperini, P. Parma, E. Gallo, N. Casati, P. Macchi *New J. Chem.* **2006**, *30*, 1046.
5. M. Gasperini, F. Ragaini *Organometallics* **2004**, *23*, 995.
6. M. Hagar, F. Ragaini, E. Monticelli, A. Caselli, P. Macchi, N. Casati, *Chem. Commun.* **2010**, *46*, 6153.
7. M. Viganò, F. Ferretti, A. Caselli, F. Ragaini, M. Rossi, P. Mussini, P. Macchi, *Chem. Eur. J.* **2014**, *20*, 14451.
8. A. Cimino, F. Moscatelli, F. Ferretti, F. Ragaini, S. Germain, J. Hannedouche, E. Schulz, L. Luconi, A. Rossin, G. Giambastiani, *New J. Chem.* **2016**, *40*, 10285.
9. D. Formenti, F. Ferretti, C. Topf, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, K. Junge, M. Beller, F. Ragaini, *J. Catal.* **2017**, *351*, 79.