

# N-Aryl Anions: Half Way between Amides and Carbanions

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A ‘carbanion’ can coordinate to a metal like an ‘amide’ if there is a nitrogen atom present to withdraw electron density from the formally negatively charged carbon center. On the other hand, shifting the negative charge from the amido nitrogen atom to the carbon substituent should convert an ‘amidic’ into a ‘carbanionic’ coordination behavior. This seems feasible with various substituents at the aromatic ring in a primary amide. This paper is concerned with the influence of aromatic substitution, as well as with the nature of the metal ion on the coordination mode of an amide ligand. Discussed are the parent lithium anilide [(thf)<sub>2</sub>LiNH(C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub> (**1**), the pentafluorinated lithium anilide [(thf)<sub>2</sub>LiNH(C<sub>6</sub>F<sub>5</sub>)]<sub>2</sub> (**2**) and the lithium amino benzonitrile [(thf)<sub>2</sub>LiNH(C<sub>6</sub>H<sub>4</sub><sup>*p*</sup>CN)]<sub>2</sub> (**3**). All amide ligands coordinate the lithium cation exclusively with their amido nitrogen atom. In the dimeric structure of **1** the atom can be regarded to be sp<sup>2</sup>-hybridized. Fluorine substitution of the ring results in a slightly more pronounced coupling of the negative charge to the aromatic ring. A *para*-nitrile group further enhances quinoidal perturbation of the C<sub>6</sub>-perimeter from six-fold symmetry. Consequently, the *ipso*- and *ortho*-carbon atoms of the ring are partially negative charged. Those carbon atoms are only attractive for the soft rubidium cation in an aza allylic coordination in [(thf)<sub>2</sub>RbNH(C<sub>6</sub>H<sub>4</sub><sup>*p*</sup>CN)]<sub>n</sub> (**4**) but not to the hard lithium cation.

*Key words:* Alkali Metals, Amides, Ligand Effects, Lithium, Rubidium