

Trifluoromethylaryl-Substituted Quinoxalines: Unusual Ruthenium-Amidinate Complexes and their Suitability for Anellation Reactions

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The reaction of the 2,3-dianilino-quinoxaline **1** with an equivalent of triethyl orthoformate results in a cyclic aminaester **2**. An excess of triethyl orthoformate results in the carbene dimer **4**. With the help of boron trifluoride, **2** can be transformed into the imidazolium salt **3**. Reaction of **1** with KOC_4H_9 leads to a quinoxaline derivative **5** under anellation of a benzene ring whereas the related pyrazino-quinoxaline **6** (formed from tetraaminobenzene tetrahydrochloride and bis-(3-trifluoromethylphenyl) oxalimidoyl chloride) does not react under similar conditions. However, **6** can be activated towards anellation by employing the complex fragment $[(\text{tbbpy})_2\text{Ru}]^{2+}$, tbbpy: bis(4,4'-di-*tert*-butyl-2,2'-bipyridine). This generates an unusual ruthenium complex **9** which could be characterised by X-ray diffraction. Complex **9** contains a pentacene derivative and coordinates the ruthenium fragment at the amidinate moiety thus forming a four-membered chelate ring. Isolation of a second ruthenium complex **8** which contains an intact pyrazino-quinoxaline **6** in which the metal is also coordinated to an amidinato group supports the assumption that the anellation reaction occurs only after metal complexation at the amidinate group. In contrast to this, the smaller $[(\text{tmeda})_2\text{Pd}]^{2+}$ fragment reacts with the pyrazino-quinoxaline **6** to form the mononuclear Pd complex **10**. Its structural motif (X-ray diffraction) shows that the palladium centre coordinates at the 1,4-diamino group of the intact pyrazino-quinoxaline to form a five-membered chelate ring. This suggests that the bulkiness of the complex fragment determines whether or not an anellation reaction can take place.

Key words: Diamino-Substituted Pyrazino-Quinoxalines, Anellation Reactions,
Ruthenium Amidinate Complexes