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Synthesis of New Functionalized Azadiene Carbonyliron Complexes

Hassan Cherkaoui, Jacques Martelli*, René Grée

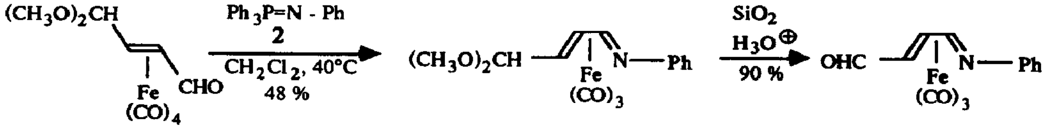
Laboratoire de Synthèses et Activations de Biomolécules, associé au CNRS
Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35700 Rennes, France

Abstract *: New carbonyliron complexes of 1-aza-1,3-dienes 3, 4 and 6 bearing an aldehyde function in position 4 are easily prepared from the fumaraldehyde complexes, 1 and 5, by aza Wittig reactions.*

Azadiene carbonyliron complexes were first described in 1967.[1] They are usually prepared by direct complexation of α,β unsaturated imines [1,2] and this reaction can be diastereoselective in the case of imines bearing a chiral substituent on nitrogen.[3] Condensation of amines with tetracarbonyliron complexes of α,β-unsaturated carbonyl derivatives is also very useful, especially in the case where the corresponding free azadienes are unknown.[4] These carbonyliron complexed azadienes are easily characterized by spectroscopic means and X-ray data indicates an η^4 complexation for the N-cinnamylidene-aniline $Fe(CO)_3$ complex.[5] However, equilibrium between π and σ bonded forms has been demonstrated in some cases.[6]

Very few studies have been reported concerning their chemical reactivity. However protonation on nitrogen,[2a] reaction with hard nucleophiles leading to a new synthesis of pyrroles, [3a] and their use as efficient transfer agents for the $Fe(CO)_3$ unit, [7] have been described. The low number of reports is probably due, at least in part, to the limited number of complexes presently accessible. As part of our program dealing with the use of carbonyliron complexes in organic synthesis,[8,9] we chose to prepare new 1-aza-1,3-diene complexes bearing an aldehyde group in position 4. This extra function is important not only in terms of structural and bonding studies but should also extend the synthetic potential of these complexes. We report here our preliminary results in this field with the synthesis and characterization of the new carbonyliron complexes 3, 4 and 6.

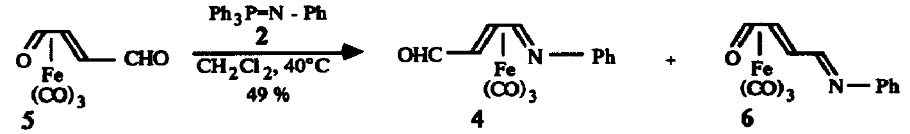
Our synthesis starts from the easily accessible carbonyliron complexes of fumaraldehyde 1 and 5 [9] and uses the aza Wittig reaction.[10] Reaction of the η^2 complex 1 with the iminophosphorane 2 (1.5 eq.) for 5 hours in anhydrous CH_2Cl_2 at 40°C gave the η^4 complex 3 (48 % yield after chromatography).



1 3 4

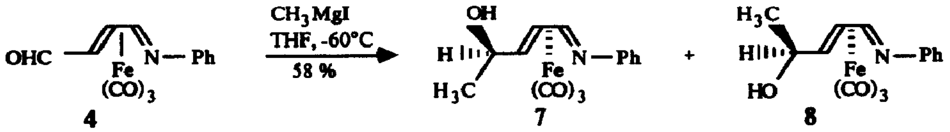
Hydrolysis of the acetal using Conia's method [11] smoothly afforded the new formyl complex 4. The structure of these complexes is easily established from spectral data [12] ; in particular the chemical shifts in the ^1H and ^{13}C NMR unambiguously establish their η^4 structures.

Under similar conditions the η^4 complex 5 reacts with 2 (1 eq.) to give a 7 : 3 mixture (49 % overall yield) of the easily isolated crystalline complex 4, as well as its more labile isomer 6 characterized only by spectral data. It is interesting to note that we could not establish an equilibrium between these two isomers. Heating either pure 4 or mixtures enriched in 6 gave only slow decomposition of these complexes and no evidence could be obtained for a possible bond shift isomerization.



It is also important to point out that none of these complexed azadienes could be obtained using the standard condensation reactions of 1 or 5 with various primary amines. *Thus, the aza Wittig reaction which has not been used before in the chemistry of carbonyliron complexes appears to be a very efficient alternative because of the neutral reaction conditions.*

In a preliminary experiment dealing with the reactivity of the free aldehyde group in 4 we established that the reaction with methyl Grignard gave a 1 : 1 mixture of alcohols Ψ-exo (more polar) 7 and Ψ-endo (less polar) 8, which were easily separated by chromatography.[13]



In conclusion, we could prepare *the first examples of functionalized* 1-aza-1,3-dienes complexed to carbonyliron moieties, by taking advantage of the mild conditions of the aza Wittig reaction. Extension to new complexes bearing other functionalized groups will provide a better understanding of the bonding properties (η^2-η^4 structures, bond shifts) of such derivatives, as well as their synthetic potential.

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12 - All new complexes have been fully characterized by their spectral and analytical or exact mass data.

13 - For explanations concerning the Ψ-exo/Ψ-endo nomenclature and relations to stereochemistry, see ref. 8 and cited literature.

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