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Inter- and intramolecular carbene reactions of diazoketones tethered to tricarbonyliron coordinated acyclic dienes. New tricarbonyliron complexes of cyclohexa-2,4-dienone and cyclopent-2-enone

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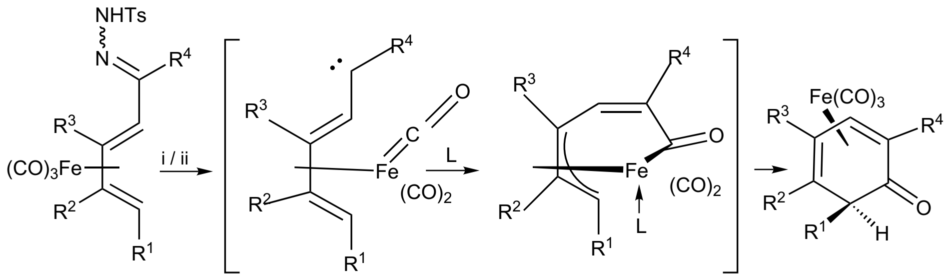
Abstract—A series of diazoketones tethered to tricarbonyliron coordinated dienes at the terminal position have been synthesized, and their decomposition reactions as carbene precursors studied. Intermolecular reactions with nucleophilic olefins were observed with Cu(acac)$_2$ as catalyst, the tricarbonyliron playing the role of an efficient protecting group of the diene fragment. With rhodium^{II} acetate, intramolecular reactions predominate, with formation of five-membered rings, in the side chain, or less commonly, as a cyclopentenone joined side by side to a rearranged diene ligand. Unusually, due to cationic stabilization by the iron, six-membered rings in the side chain are also formed here. A still different reaction was observed during the thermal decomposition of a diazoketone tethered to a coordinated diene at position 2: the formation of a stable complex of a cyclohexa-2-4-dienone (iron assisted carbene reaction and multiple hydrogen migrations).

Tricarbonyliron diene complexes are known to react easily with electrophiles.[1–3] The most studied reaction in this context is their acylation under Friedel–Crafts conditions to give complexes of linear conjugated α-dienones, two successive acylations being even possible.[4] In contrast, carbenes seem not to react readily with complexed dienes, the tricarbonyliron group playing rather the role of a protecting group for the diene, thus permitting the attack of other sites of the molecule (C=C bond,[5] activated C–H bond[6,7]), and, to our knowledge, the only intramolecular carbene reaction including a coordinated carbon atom of the diene, reported with tricarbonyliron complexes, is the cyclocarbonylation reaction, which allows the synthesis of



i: NaOMe, mesitylene (CO), 145°C
ii: 1) NaH, THF 2) mesitylene (CO), 145°C

Keywords: Diazoketone; Carbene; Tricarbonyliron; Diene; Copper; Rhodium; Cyclohexadienone; Cyclopentenodiene.

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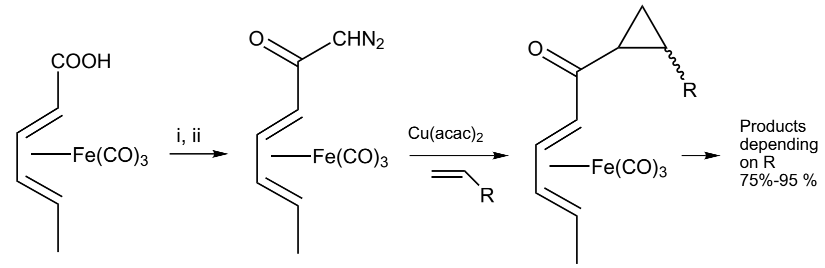
stable complexes of cyclohexadienones from precursors of acyclic α-diazodiene complexes.[8]

In this case, the carbene centre was directly adjacent to the coordinated diene, and the main reaction path was an intramolecular reaction with a CO ligand followed by ring closure within the coordination sphere of the metal.

We were now interested in carbene reactions of acyclic tricarbonyliron diene complexes where the carbene centre is tethered to the diene at position 1 or 2 by a carbon chain of variable length. Since diazocompounds are efficient carbene precursors, we have experimented with this functional group, under the form of diazoketones, which are easily obtained from the reaction of acid chlorides with diazomethane.

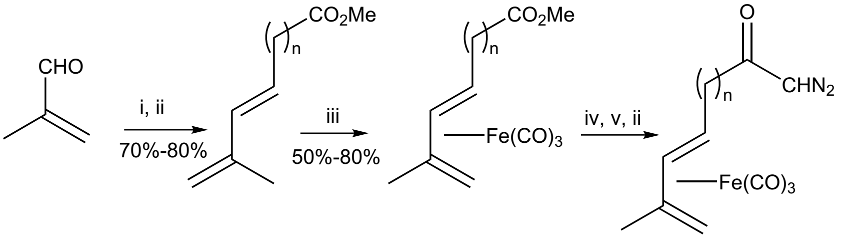
The simplest representative of that family of compounds, the diazoketone **1**, was previously synthesized and was shown to be a very efficient carbene precursor for intermolecular reactions:[9]



i : $(COCl)_2$, DMF cat.,benzene
ii : CH_2N_2, Et_2O

The high reactivity observed for intermolecular reactions with various carbene acceptors was obviously due to the fact that an intramolecular carbene stabilizing process was not competitive here, even the otherwise common Wolff rearrangement to ketenes.

The next homologous diazoketone **2**–**4**, with carbon chain spacers of 2, 3 and 4 atoms ($n = 2$–4), were prepared by Wittig reactions on methacrolein to give isoprenic acids, which were complexed as esters, followed by saponification,[10] transformation into the acid chlorides, and finally reaction with diazomethane.[11]

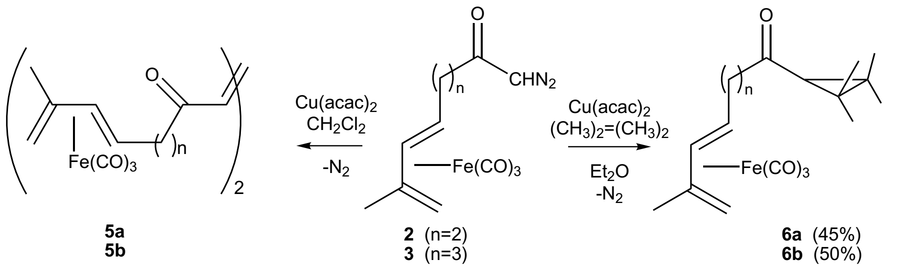


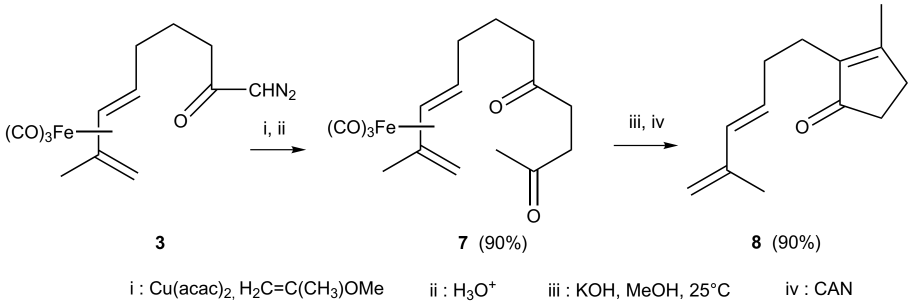
i : $Br(C_6H_5)_3P(CH_2)_{n+1}CO_2H$, LiHMDS, THF
ii : CH_2N_2, Et_2O
iii : $Fe_2(CO)_9$, pentane, 35°C
iv : KOH / H_2O, EtOH
v : $(COCl)_2$, DMF cat.,benzene

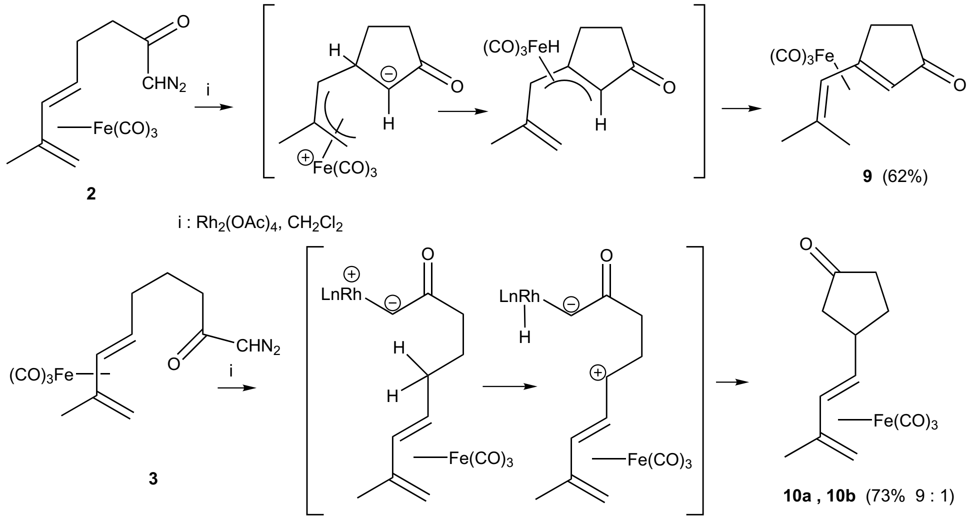
n = 2 **2** (60%)
n = 3 **3** (65%)
n = 4 **4** (55%)

By heating without any catalyst, these diazoketones were stable up to 100 °C, and above gave only mixtures of products, which were difficult to separate and to identify (inter alia ca. 15% CH-insertion products with the solvent, when refluxing in mesitylene). The decomposition was already effective at 25 °C, when catalyzed by $Cu(acac)_2$ but the carbene dimers **5** were the main products, in dichloromethane (ca. 30% isolated) or in benzene (ca. 40% isolated). In presence of nucleophilic olefins as carbene acceptors, only intermolecular additions were observed, the tricarbonyliron playing the role of an efficient protecting group for the diene fragment. This allowed therefore the synthesis of cyclopropanic products such as **6**, or transformed cycloaddition products in high yields, such as the diketone **7** and the cyclopentenone **8** after decomplexation, which would not be obtained without this protection.[12]

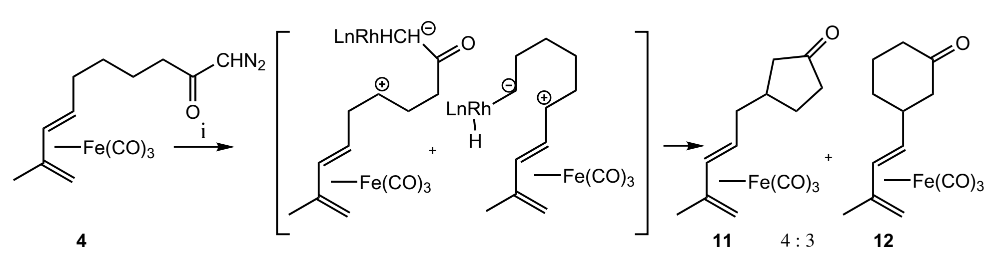
The situation changed completely when Rh^{II} was used as catalyst, in dichloromethane at room temperature, leading now to intramolecular reaction products, with different outcomes for the diazoketone **2** and the diazoketone **3**. The complexed dienyl diazoketone **2**, with a 2 carbon chain between the diene and the diazoketone carbonyl, gave as main product the cyclopentenodiene complex **9** (isolated 62%). The formation of this cyclopentenone, whose double bond is a part of the new dienic ligand, results probably from a direct attack of the carbene on the nearest terminal carbon atom of the complexed diene, with formation of a coordinatively unsaturated π-allyl iron cation intermediate. Stabilization by hydride abstraction to a 18 electrons hydrido-iron complex, followed by hydrogen transfer leads then to **9**.[13] The diazoketone **3** ($n = 3$) led also to the formation of five membered rings, but the cyclopentanones **10a** and **10b** obtained with a relatively high diastereoselectivity (73%, 9:1), are the result of CH insertion reactions, apparently favoured here by the formation of iron-stabilized zwitterionic intermediates (zwitterionic mechanism[14]):





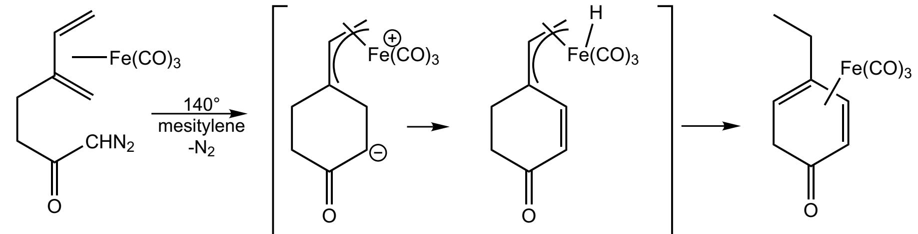


An argument for such a stabilization is given in the relatively high proportion of six-membered ring formed in the reaction of the diazoketone **4**, with a 4 carbon atom spacer (**11**:**12** = 4:3; 45%), since usually five membered rings are highly preferred in Rh catalyzed CH insertion reactions:[15]



i : Rh$_2$(OAc)$_4$, CH$_2$Cl$_2$

When the diazoketone side chain was attached to the diene ligand at position 2, one could expect that a carbene reaction would occur at the reactive terminal position of the coordinated diene, at least for favourable chain length. This was actually observed with the diazoketone **13**,[16] which gave by thermal decomposition a



13 **14**

six-membered ring, leading after multiple iron assisted hydrogen migrations to a stable tricarbonyliron complex of a cyclo-2,4-hexadienone, **14** (isolated 40%).[17]

Acknowledgements

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11. In the IR (CCl$_4$), the characteristic strong absorptions ν (C=O) and ν (N$_2$) of the diazoketones **2**–**4** and **13** are close to 1650 and 2110 cm^{-1}, with the strong carbonyl-ligand absorptions near 1960–1970 cm^{-1} and 2050 cm^{-1}.
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16. The diazoketone **13** was prepared by reacting diazomethane with the corresponding acid chloride, obtained from the known complex of the acid[18] (Oxalyl chloride 10 equiv, DMF 0.1 equiv in Bz at 20 °C, followed by treatment with an excess CH_2N_2 in ether added at 0–20 °C, 93% from the acid complex).
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