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Preliminary Note

o-Lithiotetrafluorophenylcyclopentadienyliron dicarbonyl: a polyfluoroaryl-lithium derivative, thermally stable against intramolecular lithium fluoride elimination

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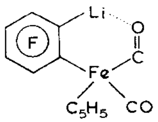
The elimination of lithium fluoride from polyfluoroaryl-lithium derivatives is well documented[1]. In our current investigations[2,3] into the isomeric bromotetrafluorophenylcyclopentadienyliron dicarbonyls, we have found all three isomers to undergo lithium/bromine exchange with n-butyl-lithium, the corresponding hydrotetrafluorophenyl derivative being formed after addition of water at −78°. Both the *meta*- and *para*-lithium species react with cyclopentadienyliron dicarbonyl iodide to give the corresponding bis(cyclopentadienyliron dicarbonyl)tetrafluorobenzene. The *ortho*-lithium derivative, however, gave only the *ortho*-hydro derivative and the non-formation of the bis-iron derivative was initially explained by unfavorable stereochemistry.

In the presence of furan, the lithium derivatives of the *meta* and *para* compounds produce[4] the expected Diels–Alder addition products from a benzyne + furan type reaction. The *ortho*-lithium species, however, gave only the *ortho*-hydrotetrafluorophenyl compound.

The *ortho*-lithium species was allowed to reach room temperature without the addition of furan, and then stirred for 24 h. Again, only the *ortho*-hydrotetrafluorophenyl derivative was produced in almost quantitative yield. The same reaction, but with addition of D_2O, did not produce any of the corresponding *ortho*-deuterotetrafluorophenyl derivative. When D_2O was added to an equimolar mixture of the *ortho*-bromotetrafluorophenyliron derivative and n-butyl-lithium that had been stirred for 2 h at −78°, a quantitative yield of *ortho*-deuterotetrafluorophenylcyclopentadienyliron dicarbonyl was obtained, thus verifying the actual formation of the *ortho*-lithium derivative. In a subsequent experiment, addition of D_2O to a reaction mixture that had been allowed to stir at room temperature for 4 h produced a mixture of the deutero and hydro derivatives. The two species were clearly indicated by mass spectral data.

It is thus apparent that we do have a tetrafluorophenyl-lithium derivative that is thermally stable against intramolecular lithium fluoride elimination, but unstable with respect to lithium/hydrogen exchange over a period of time. The source of the hydrogen atoms is somewhat strange, and the very high yield of product rules out participation of the cyclopentadienyl group from another molecule. This leaves the diethyl ether solvent, hexane (in which the n-butyllithium is obtained) and the n-butyl bromide produced in the lithiation step. Analogous lithium/hydrogen exchange has not been observed for the *meta*- and *para*-lithium derivatives.

It seems conceivable that the lithium atom is somehow being "tied-down" by the presence of the cyclopentadienyliron dicarbonyl group, and a possible heterocyclic lithium–oxygen-bonded intermediate of the following structure is a distinct possibility:



Infrared spectroscopic studies are currently in progress to attempt to verify the above type of structure.

REFERENCES

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