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Novel Alkylidenating Agents of Iron(III) Derivatives by Base-Mediated α,μ-Dehydrohalogenation and Their Chemical Trapping by Cycloaddition[‡]

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Dedicated to Professor Dr. Uwe Rosenthal on the occasion of his 60th birthday

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Studies of the reactions between group 4 metal chlorides (M = Ti, Zr, Hf) and methyllithium at –78 °C in toluene can lead to methylidene–metal complexes, $H_2C{=}MCl_2$, by a sequence of monomethylation, α-carbon lithiation and α,μ-elimination of LiCl. Here study of the preparation of alkylidene derivatives of iron was attempted by the interaction of $FeCl_3$ with *n*-butyllithium in various ratios at –78 °C. The presence of any resulting butylidene–iron(III) derivative, *n*PrCH=FeE (E = Cl, *n*Bu), was probed by adding chemical trapping agents, such as diphenylacetylene, benzonitrile, methyl benzoate and benzophenone. In each experiment the hydrolyzed products were consistent with a cycloaddition reaction of *n*PrCH=FeE with the trapping agent. The products from diphenylacetylene and from benzonitrile with D_2O workup are uniquely in accord with such a carbene precursor. A 3:1 ratio of *n*BuLi/$FeCl_3$ gave the optimal yield of *n*PrCH=Fe*n*Bu, ca. 80 %, from the $n\mathrm{Bu}_2\mathrm{FeCl}$ precursor. When a 3:1 reaction mixture was simply brought to 25 °C and hydrolyzed, the purple alkylidene–iron complex decomposed completely to iron metal. A study of a 3:1 interaction of $PhCH_2MgCl$ and $FeCl_3$ under similar conditions and trapping with diphenylacetylene provided evidence for the formation of PhCH=Fe–CH_2Ph in ca. 40 %. These results support the hope that alkylidene–iron(III) analogs of the Grubbs reagents may be accessible by this process.

Introduction

The formal complexation of a Lewis-acidic carbene **1** with a transition metal compound **2**, of variable oxidation state and having unshared d-electrons, can lead to transition metal–carbenes **3** [Equation (1)].[2] The broad utility of such metal–carbenes in organic synthesis, in industrial hydrocarbon transformations and in specialized polymerizations has spurred the preparation of diverse metal–carbenes from almost all transition metals. Their individual applications in synthesis range from carbonyl olefination with titanium reagents of the Tebbe type, $Cp_2Ti{=}CR_2{\cdot}M_mX_n$,[3,4] through cyclopropanation with cationic iron complexes of the Fischer[5] type, $[Cp_2(CO)_2Fe{=}CR_2]^+$, to olefin metathesis or ROMP polymerization Grubbs catalysts[6] of ruthenium, $[Cl_2(Ph_3P)_2Ru{=}CHR]$, and of the Schrock[7] molybdenum type, [(RO)(ArN)Mo=CHR]. The scientific impact of such structurally defined carbene complexes was recognized by the joint award of the Nobel prize to Grubbs and Schrock in 2005, along with an equal share to Chauvin for his insight into the metallacyclobutane intermediate involved in metathesis.

The great versatility of Grubbs catalysts has led us to explore whether similar metathesis catalysts based on inexpensive iron reagents could be developed. Therefore, we have examined the interaction of iron(III) chloride with organolithium and organomagnesium reagents in THF at low temperatures (Scheme 1). Many previous attempts to isolate or to detect alkyliron(III) intermediates at or near room temperature, in the absence of special stabilizing ligands, have failed.[8] Some success in generating alkyliron(II) species in situ, such as MeFeCl, Me_2Fe and $n\mathrm{Bu}_4\mathrm{FeLi}_2$, has been achieved, and these reagents have proved valuable in effecting cross-coupling with 1-alkenyl halides.[9]

In such a proposed reaction we expected that the dialkylated intermediate **4** would be formed readily. But in further attempted alkylation to form $(RCH_2)_3Fe$, steric hindrance might be expected to favor the carbene **5**, by a process we have found to occur between the early transition metal compounds, $TiCl_4$ and $ZrCl_4$, with CH_3Li, namely, α,μ-dehydrohalogenation, leading to $H_2C{=}MCl_2$.[10] Therefore, in the following study we carried out the reactions in Scheme 1 at –78 °C and thereafter proposed to trap chemically iron–carbenes **5** with reagents such as alkynes, nitriles and

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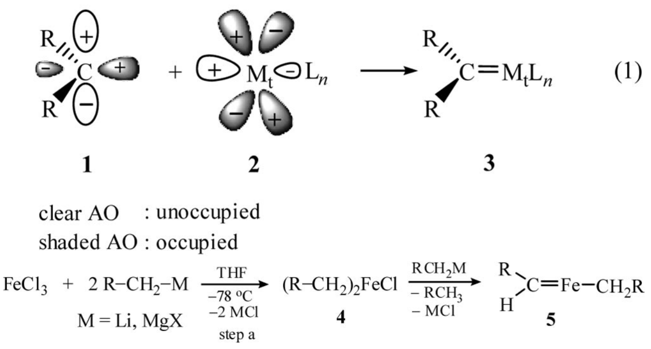


Scheme 1.

carbonyl derivatives by cycloaddition, a reaction of transition metal carbenes well-precedented with those of group 4.[10,11a,11b]

Results

General Overview and Empirical Categorizations of the Results

From the interaction of 1:3 molar ratios of $FeCl_3$/*n*-butyllithium at –78 °C the anticipated products were tri-*n*-butyliron(III) (**6**), nBu_3Fe, with its β-elimination of 1-butene derivative, nBu_2Fe–H or the reduction product nBu_2Fe, and its possible carbene, *n*-butyliron(III)–butylidene (**7**), *n*Bu–Fe=CH–*n*Pr. In summary, three categories of results with the trapping agents were observed. Category 1 consists of the reactions of diphenylacetylene (**8**) or benzonitrile (**18**) with the 1:3 $FeCl_3$/*n*BuLi reaction mixture, with or without workup with D_2O or aqueous DCl: such reactions were uniquely interpretable in terms of cycloaddition trappings of **7**, as depicted in Schemes 2 and 4. The ratio of **6**/**7** generated in the reaction mixture was estimated at 20:80. Category 2 consists of the reactions of methyl benzoate (**22**) or benzophenone (**24**), with or without attempted deuteriolysis. These results were consistent with cycloaddition trappings of **7** but lack the detection of deuteriated intermediates in high yield expected from Schemes 5 and 6. Category 3 are the reactions of benzyl chloride or (*E*)-stilbene oxide with the 1:3 $FeCl_3$/*n*BuLi mixture, which proceeded well to give 97% of bibenzyl and 3% of toluene or 85% of (*E*)-stilbene, respectively. But the nature of the products did not permit any distinction between the presence of **6** or **7**. Therefore, such reactions will be deferred to future study.

Consideration of certain stereochemical and deuteriolytic aspects connected with Categories 1 and 2 will be treated in the Discussion.

Reaction of Iron(III) Chloride with *n*-Butyllithium

1:3 Molar Ratio of $FeCl_3$/nBuLi

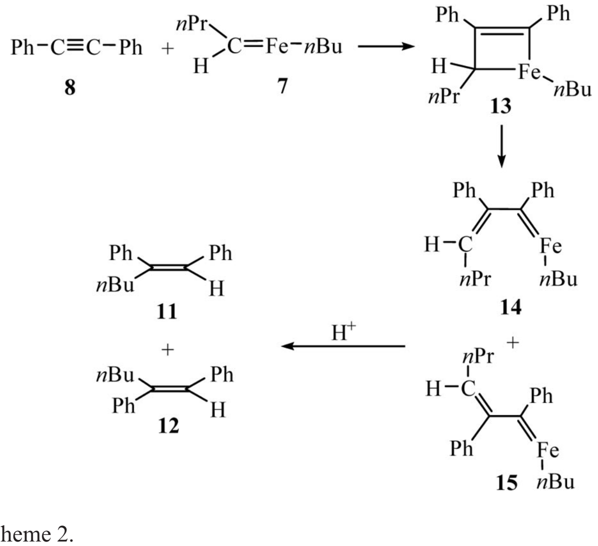
(1) Simple Hydrolytic Workup

When the reaction was conducted in THF at –78 °C with a 1:3 molar ratio of $FeCl_3$/*n*BuLi, a purple reaction mixture resulted. When such a mixture was gradually brought to 25 °C, a black suspension was formed and coated the magnetic stirbar. Since this black solid readily dissolved in aqueous HCl with evolution of H_2, it can be assumed that it was iron powder.[11c] If any tri-*n*-butyliron (**6**) or *n*-butyliron(III)–propylidene (*n*Bu–Fe=CH–*n*Pr, **7**) were formed at –78 °C, it is evident that they decomposed to radicals and iron.

*(2) Reaction with Diphenylacetylene (**8**)*

To the preformed mixture of 1:3 ratio of $FeCl_3$/*n*BuLi at –78 °C was added 0.93 mol-equiv. of diphenylacetylene in hexanes and the reaction mixture treated further and hydrolyzed as in section 1. The hydrolyzed products consisted of (*Z*)-stilbene (**9**, 8%), (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**10**, 10%), (*Z*)-1,2-diphenyl-1-hexene (**11**, 18%) and (*E*)-1,2-diphenyl-1-hexene (**12**, 64%).

Therefore, the formation of isomeric **11** and **12** as the major hydrolysis products is uniquely in accord with the presence of iron–carbene **7** in the reaction mixture (Category 1). Capture of **7** by cycloaddition with **8** would yield **13**. Electrocyclic ring-opening of **13** would produce an equilibrated conformational mixture of **14** and **15**, whose subsequent hydrolysis would lead to the observed mixture of **11** and **12**. Steric factors would favor the (*E*)-iron–carbene **15** and its hydrolyzed counterpart **12** (Scheme 2). (In Scheme 2 and successive schemes substituents on chiral carbon atoms will be shown with solid lines, which indicate the stereochemistry is undefined.)



Scheme 2.

The minor products **9** and **10** can be readily explained by the formation of an iron–hydride linkage by β-elimination of 1-butene from any **6** (nBu_3Fe) present or from **7** itself. Hydroferration of **8** and insertion of **8** into adduct **16** seem to be the minor pathway leading to the formation of **17** (Scheme 3). (Cf. further consideration in the Discussion.)

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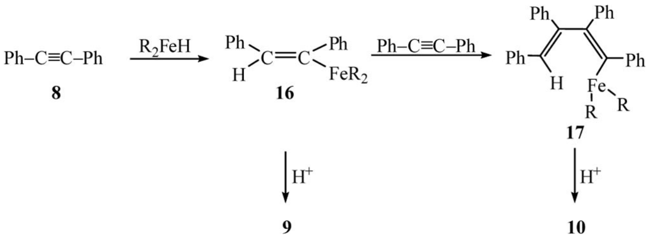
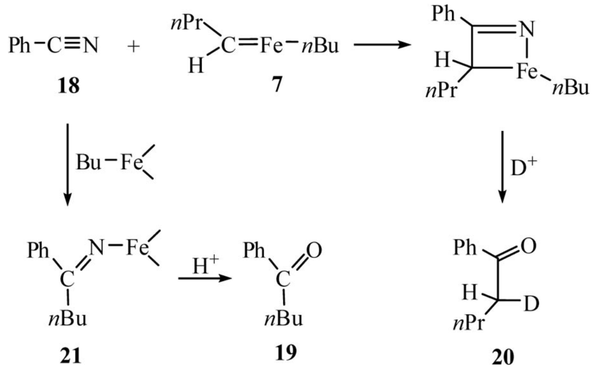


Scheme 3.

*(3) Reaction with Benzonitrile (**18**)*

Similar to the procedure in section 2, the $FeCl_3$/*n*BuLi mixture (1:3) was treated with 0.93 mol-equiv. of benzonitrile (**18**) and worked up by hydrolysis. The sole product was valerophenone (**19**) in 98% yield.

When an identical reaction run was worked up with 1 N DCl in D_2O (98%), the resulting valerophenone was found to be 75% monodeuteriated at the α-carbon center (**20**). Therefore, this observation is uniquely in accord with the principal reaction path being via iron–carbene **7** (Scheme 4) (Category 1).

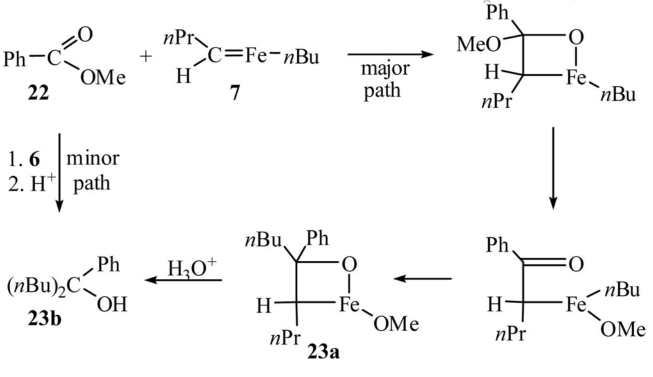


Scheme 4.

The undeuteriated **19** could be attributed to minor, direct butylation of **18** via **21**.

*(4) Reaction with Methyl Benzoate (**22**)*

As in sections 2 and 3, the $FeCl_3$/*n*BuLi mixture (1:3) was treated with 0.93 mol-equiv. of methyl benzoate (**22**). Workup gave a quantitative yield of 5-phenyl-5-nonanol (**23b**). Since the foregoing reactions with **8** and **18** indicated that over 80% of the reaction products were consistent with presence of iron–carbene **7**, the following path must be the principal route to **23** (Scheme 5). Because of the involvement of butyl–iron bonds in a minor reaction path for sections 2 and 3, it can be concluded that 15–20% of the **23b** formed resulted directly from a butyliron–alkyl species, such as **6**.



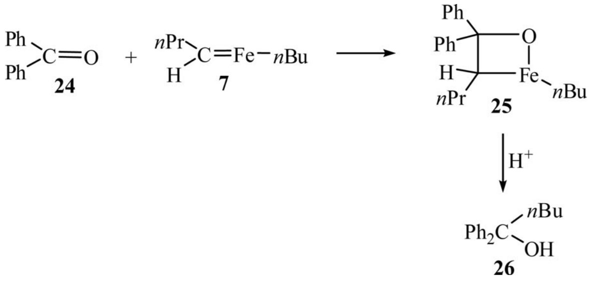
Scheme 5.

In the attempt to further support the role of **7** in the major path, an identical reaction run was worked up with 1 N DCl in D_2O with the hope of detecting a deuteriated derivative of **23b**. However, by ^1H NMR spectroscopy **23** had little (ca. 10%) deuteriation at the α-CH_2 of the butyl group. Hence, this reaction is placed in Category 2. However, the tendency of neutral, high-valent σ-bonded alkyl transition metal species to undergo homolysis above 0 °C may mean that **23a** might not survive at the deuteriolysis temperature (cf. Discussion). Note the complete homolytic cleavage of C–Fe bonds in the purple reaction mixture when brought above 0 °C for hydrolysis (section 1).

*(5) Reaction with Benzophenone (**24**)*

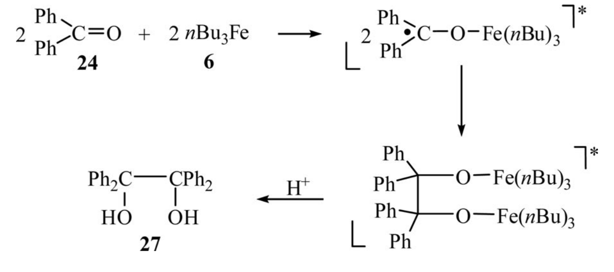
As in the foregoing procedures, the $FeCl_3$/*n*BuLi mixture (1:3) was treated at –78 °C with 0.93 mol-equiv. of benzophenone (**24**). Hydrolysis of the reaction mixture gave as products 1,1-diphenyl-1-pentanol (**26**, 78%) and benzhydrol (**27**, 22%).

Again, the main product **26** can be attributed to a cycloaddition of **7** to **24** to yield **25**. Hydrolysis would then produce **26** (Scheme 6). An attempt to detect **25** by deuteriolytic workup, as in section 4, was also inconclusive. The α-CH_2 of the butyl group in **26** showed by ^1H NMR analysis <20% of CHD. Thus, this experiment falls into Category 2, and the similar failure of deuteration deserves further consideration (cf. Discussion).



Scheme 6.

The minor product could arise from a pinacol coupling induced by the small amounts of alkyliron species **6**, itself a free radical (Scheme 7). The bracketed structures (*) are suggested, without evidence, as transitory intermediates in such C–C bond coupling.



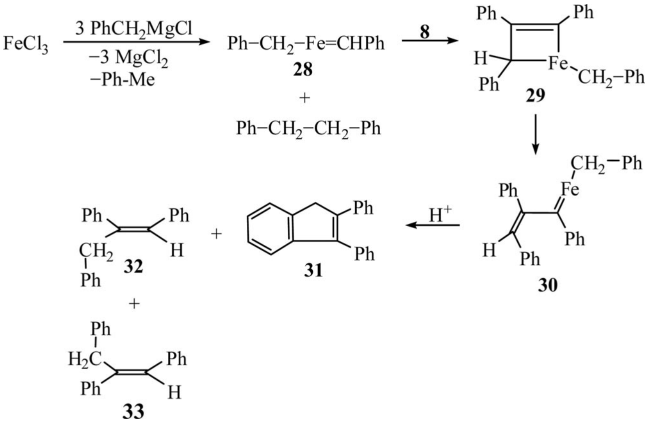
Scheme 7.

When this reaction was attempted by adding the benzophenone at 25 °C, 98% of **24** was recovered, and only a trace of tetraphenylethylene was detected.

Reaction of Iron(III) Chloride with Benzylmagnesium Chloride

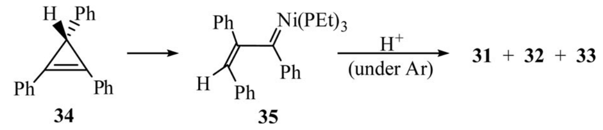
When 1 mol-equiv. of iron(III) chloride in THF was allowed to react with 3 mol-equiv. of benzylmagnesium chloride at –78 °C and the mixture then warmed to 25 °C, a black suspension was ultimately formed. The black solid, which coated the magnetic stirbar, dissolved in aqueous HCl with the evolution of H_2 and thus was iron powder.[11c]

The foregoing reaction was carried out again, but this time the iron(III) chloride was first admixed with 0.93 mol-equiv. of diphenylacetylene (**8**) at –78 °C before the 3 mol-equiv. of benzylmagnesium chloride were added. Similar further reaction and hydrolysis led to a mixture of bibenzyl (49%), 2,3-diphenylindene (**31**, 7%), (*Z*)-1,2,3-triphenyl-1-propene (**32**, 17%) and (*E*)-1,2,3-triphenyl-1-propene (**33**, 17%). The origin of **31**–**33** can be attributed to the generation of Ph–CH$_2$–Fe=CHPh (**28**) in the reaction mixture and its capture by its cycloaddition to **8** with the formation of **29**. Electrocyclic ring-opening of **29** would then produce **30**. Protonation of this carbene would yield **31**–**33** (Scheme 8).



Scheme 8.

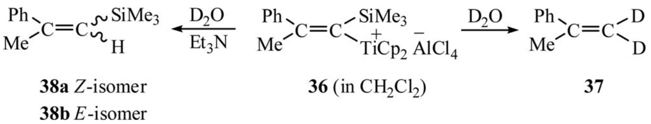
The unusual protonation of iron–carbene **30** to yield **31**, **32** and **33** finds its exact precedent in the reaction of 1,2,3-triphenylcyclopropene (**34**) with $(Et_3P)_4Ni$.[12] From this interaction the nickel–carbene **35**, analogous to **30**, is thought to form.[13] Here again, protolysis of **35** yields **31**, **32** and **33** (Scheme 9).



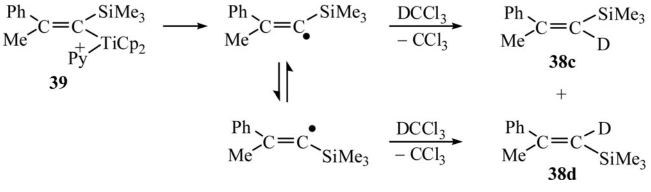
Scheme 9.

Discussion

From the foregoing reaction of iron(III) chloride in THF with *n*-butyllithium at –78 °C in a 1:3 molar ratio, all the results are consistent with formation and reactions of two organoiron intermediates in about an 80:20 ratio. The major product has the chemical properties consistent with an iron–carbene of the structure *n*Bu–Fe=CH–*n*Pr (**7**),[14] namely the cycloaddition reaction,[11] whereas the minor reagent undergoes different reactions with an array of substrates consistent with an *n*-butyliron(III) intermediate, most likely of the structure $(nBu)_3Fe$ (**6**).[14] One discordant observation in interpreting this body of results in terms of cycloaddition reactions of iron–carbene **7** is the failure to detect organoiron intermediates **23a** and **25** by deuteriation in high yields of **23b** and **26**. But similar failure is encountered with titanium derivatives of the structure **36** (verified by X-ray analysis.[15]). Direct treatment of **36** in CH_2Cl_2 with D_2O cleaved both C–M bonds with the quantitative formation of **37** (Scheme 10). However, when **36** was treated first with excess Et_3N, then a 50:50 mixture of completely protonated (*Z*) and (*E*) isomers of **38** was obtained (**38a** and **38b**). Subsequently, it was shown that when a solution of **36** in $CDCl_3$ was treated with a pyridine/water mixture, the (*Z*) and (*E*) isomers obtained were 84% deuteriated as **38c** and 71% deuteriated as **38d**, respectively. These results clearly indicate an induced homolysis of the pyridine complex **39** before protolysis[16] (Scheme 11).



Scheme 10.

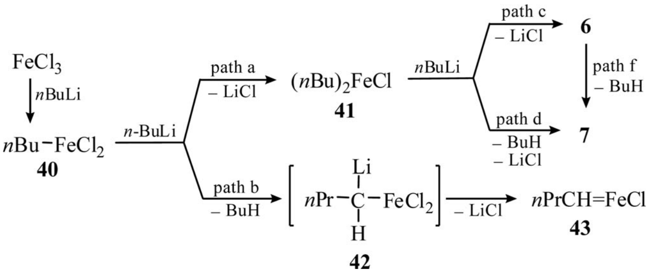


Scheme 11.

By analogy we propose that iron intermediates **23a** and **25** largely undergo homolysis before the deuteriolysis step with the resulting organic radicals abstracting hydrogen atoms from THF.

As to the cycloaddition proposed to occur between **7** and diphenylacetylene, one should consider whether alternative modes of forming products **11** and **12** might be competitive. Both such involve the carbometallation of the C≡C bond, either by *n*-butyllithium itself at –78 °C or by an *n*-butyliron reagent, such as **6**. Both alternatives can be rejected based on known reactions. *n*-Butyllithium adds to diphenylacetylene exclusively in an (*E*) manner, leading only to **12**.[19] Were this so, the origin of **11** would be unexplained. As to the possible addition of an *n*-butyl–iron bond from **6**, in the whole of transition metal chemistry there appears to be no example of a butyl–metal bond carbometallating a C=C or C≡C linkage. What occurs preferentially is the loss of 1-butene and the hydrometallation of the unsaturated C–C bond, as proposed in Scheme 3.

A unifying network proposing the likely origin of **6** and **7** and their possible relationship to each other is offered in Scheme 12. The actual paths of the depicted reactions can be delimited by the reaction of $FeCl_3$ with *2* mol-equiv. of *n*-butyllithium. Simple butylation of **40** by chloride displacement would lead to **41** (path a), but α-lithiation of **40** would produce **42**, and α,μ-elimination would then generate **43** (path b) (Scheme 12). A decisive distinction between these two pathways was made by adding *1* mol-equiv. of methyl benzoate (**22**) to the reaction mixture. Workup provided a quantitative yield of 5-phenyl-5-nonanol (**23b**) (Scheme 5). Since **41** is the only organoiron reagent present having *two* C_4 groups available (**43** having only *one* C_4 group), the reaction of **40** with *n*BuLi must have proceeded only by path a.



Scheme 12.

The further reaction of **41** with the third equivalent of *n*BuLi could have led to **6** by path c, involving butylation of **41** with chloride displacement or produced **7** by path d through a sequence of α-lithiation and α,μ-elimination, similar to path b. Alternatively or competitively, **7** might have formed from **6** (paths c and f). Although a compelling choice cannot yet be made, we favor the simplicity of path d leading to **7**, for whose intermediates cogent evidence has been adduced with alkyl group 4 compounds.[10]

Similarly, preliminary experiments herein reported with the organylation of iron(III) chloride by benzylmagnesium chloride support the generation of intermediate iron(III)–carbenes, such as benzyliron(III)–benzylidene (**28**) in moderate yields (Scheme 8). Since such relatively inexpensive iron(III)–carbenes would be direct structural analogs of the versatile and highly valuable ruthenium–carbenes of the Grubbs catalyst, our future research will be focused on generating such iron–carbenes selectively and in high yield and in isolating these carbenes with stabilizing phosphanes or N-heterocyclic carbenes.[17]

Conclusions

The interaction of a 1:3 ratio of $FeCl_3$/*n*-butyllithium in THF at –78 °C forms a purple solid containing about an 80:20 mixture of *n*-butyliron(III)–butylidene (**7**)/tri-*n*-butyliron(III) (**6**), whose presence was uniquely in accord with chemical trapping results obtained with diphenylacetylene or benzonitrile, augmented by deuteriolysis. Further trapping with methyl benzoate or benzophenone gave products completely consistent with the presence of **7** but deuteriolysis gave low deuteriation of the products. Because of the low stability of any C–Fe bond above 0 °C, such organoiron intermediates most likely underwent homolysis before reacting with D_2O in the workup. Similar results with the 1:3 interaction of $FeCl_3$ and benzylmagnesium chloride support the generation of benzyliron(III)–benzylidene (**28**) in moderate yield.

Experimental Section

Instrumentation, Analysis and Starting Reagents: The *n*-butyllithium (1.6 M in hexane) and the iron(III) chloride (anhydrous, 97%) were used as received from Aldrich Chemical Company. All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal/benzophenone ketyl mixture prior to use.[18] The IR spectra were recorded with a Perkin–Elmer instrument (model 457), and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^1H and ^{13}C) were recorded with a Bruker spectrometer (model EM-360), and tetramethylsilane (Me_4Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me_4Si reference signal. The GC/MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett–Packard 5970 mass-selective-detector instrument. The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-30 capillary column. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected.

Reactions of Iron(III) Chloride with *n*-Butyllithium

General Reaction Procedure and Hydrolytic Workup: All glassware and needles for the transfer and reaction of liquid samples were dried in an oven at 120 °C and while cooling were thoroughly flushed with argon. The standard reaction apparatus was a 125-mL, two-necked Schlenk flask, provided with a Teflon-coated stirbar and having the argon inlet on one neck and a rubber septum on the other neck. Then 50 mL of the anhydrous, deoxygenated solvent (generally THF or occasionally hexane was introduced and afterwards the content of a 5.00 g-bottle of commercial, powdered and anhydrous iron(III) chloride (97%, 30.0 mmol) was emptied into the flask under a stream of emerging argon. The reaction suspension was cooled to –78 °C with magnetic stirring. Thereupon,

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2 or 3 mol-equiv. of 1.60 M *n*-butyllithium in hexanes (38 mL or 56 mL) were added dropwise by syringe through the septum. The resulting dark purple mixture was stirred at –78 °C for 3 h. In most reactions, the reaction mixture at –78 °C was then treated with 28.0 mmol of the chemical derivatizing reagent dissolved in anhydrous, deoxygenated hexanes through the rubber septum with a gastight syringe. The resulting mixture was warmed to 25 °C over 15 h, during which time the purple reaction color turned black. Hydrolysis of the mixture with 1 N aqueous HCl (or with D_2O), extraction with three 20-mL portions of diethyl ether and combination of the diethyl ether extracts gave an organic solution, which was washed with aqueous $NaHCO_3$ and then dried with anhydrous Na_2SO_4. Removal of volatiles left an oil in good mass recovery (ca. 95%), which was analyzed directly by NMR and IR spectroscopy. In any attempted deuteriolytic workup the stirred reaction mixture was warmed up to 0 °C in an ice bath and treated dropwise from a gastight syringe, first with 5 mL of D_2O (98%) and then with 5 mL of 1 N DCl in D_2O. After deuteriolysis, a normal hydrolytic workup was conducted.

Reactions of Iron(III) Chloride with 2 mol-equiv. of *n*-Butyllithium and Subsequent Chemical Treatments: This reaction could occur in two principally different ways (cf. Scheme 12): either (1) to form $n\mathrm{Bu_2FeCl}$ (**41**); or (2) to generate carbene **43** by α,μ-dehydrohalogenation from **42**. The reaction of $FeCl_3$ in hexanes with 2 mol-equiv. of *n*-butyllithium was carried out at –78 °C according to the general procedure, and then various runs were treated with 0.28 mmol of the following reagents. Hydrolytic workup gave the following results.

(1) Methyl Benzoate (22): Usual workup gave essentially a quantitative yield (6.30 g) of relatively pure 5-phenyl-5-nonanol (**23b**). ^{1}H NMR ($CDCl_3$): δ = 0.82 (m, 6 H), 1.05 (m, OH), 1.25 (m, 6 H), 1.80 (m, 6 H), 7.20–7.45 (m, 5 H) ppm (overlapping multiplets). ^{13}C NMR ($CDCl_3$): δ = 13.93 (CH_3), 22.416 (CH_2), 25.56 (CH_2), 42.683 (CH_2), 57.0 (quaternary C), 125.2, 126.3, 127.7 and 133.0 (phenyl C) ppm. Since the formation of **23b** from methyl benzoate (**22**) requires 2 equiv. of *n*-butyl groups, the iron intermediate involved here must be $n\mathrm{Bu_2FeCl}$ (**41**), rather than **43**.

(2) Benzophenone (24): After the ketone in hexanes was added and the mixture stirred at 20–25 °C for 18 h, the color changed from dark purple to brown. Usual hydrolytic workup gave an organic residue of 82% of 1,1-diphenyl-1-pentene and 18% of 1,1,2,2-tetraphenyl-1,2-ethanediol (**27**). ^{1}H NMR of 1,1-diphenyl-1pentene ($CDCl_3$): δ = 0.86 (t, CH_3), 1.40 (sext, CH_2–CH_2), 2.10 (q, CH_2), 6.12 (t, CH), 7.15–7.40 (m, 10) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.03 (CH_3), 36.95 (CH_2), 43.882 (CH_2), 64.1 (CH), 126, 127, 128, 128.5, 141 ppm. ^{1}H NMR of 1,1,2,2-tetraphenyl-1,2-ethanediol ($CDCl_3$): δ = 2.4 (s, 2 H), 6.9–7.3 (m, 20 H) ppm.

(3) Benzophenone (24) at 25 °C: After the reaction of $FeCl_2$ in hexane suspension with 2 mol-equiv. of *n*-butyllithium was conducted at –78 °C, the purple reaction mixture was brought to 25 °C. Within 24 h at this temperature the mixture had turned black. Then benzophenone (5.1 g, 0.28 mmol) in dry THF (15 mL) was added. After 2 h, usual hydrolytic workup with 1 N aqueous HCl caused gas evolution from a gray solid coating the stirbar (likely Fe). The layer was found to contain >95% of benzophenone with only traces of benzhydrol and tetraphenylethylene.

Reactions of Iron(III) Chloride with 3 mol-equiv. of *n*-Butyllithium with Subsequent Chemical Derivatization: By means of appropriate chemical trapping reagents a clear distinction between the two proposed reaction pathways in Scheme 10, paths a and c vs. paths a and d, was sought. The generation of $n\mathrm{Bu_3Fe}$ (**6**) should be indicated by its alkylating or hydrometallating action on organic substrates. On the other hand, iron–carbene **7** should signal its presence by its characteristic cycloadditions with strained olefins, alkynes or nitriles. The reaction of $FeCl_3$ in hexanes with 3 mol-equiv. of *n*-butyllithium was carried out at –78 °C according to the general procedure, and then various runs were treated with 28 mmol of the following reagents.

(1) Methyl Benzoate (22): A quantitative yield of 5-phenyl-5-nonanol resulted. Vide supra for ^{1}H and ^{13}C NMR spectroscopic data.

(2) Benzophenone (24) at –78 °C: A mixture of 1,1-diphenyl-1-pentanol (**26**, 78%) and benzhydrol (22%) resulted, as shown by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR of **26** ($CDCl_3$): δ = 0.86 (t, CH_3), 2.13 (m, CH_2–CH_2), 2.23–2.28 (t, 2 H), 7.25–7.50 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 23.05 ($\mathit{C}H_2$–CH_3), 25.09 ($\mathit{C}H_2CH_2CH_3$), 32.5 [$\mathit{C}H_2(CH_2)CH_3$], 126.0–129.0 (4 ArC) ppm. ^{1}H and ^{13}C NMR spectra of benzhydrol were identical with the known spectra.

(3) Benzophenone (24) at 25 °C: When the benzophenone was added to such a reaction mixture brought to 25 °C, ca. 98% of **24** was recovered, and a trace of tetraphenylethylene was formed.

(4) Benzonitrile (18): After addition of **18** at –78 °C, usual reaction, hydrolytic workup and column chromatography, valerophenone (440 mg, 98%) was isolated. ^{1}H NMR of **19** ($CDCl_3$): δ = 0.93 (t, CH_3). 13.5 (sext, 2 H), 1.71 (quint, 2 H), 2.96 (t, 2 H), 7.42–7.46 (m, 2 H), 7.52–7.56 (m, 1 H), 7.94–7.97 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.09, 22.65, 26.63, 38.48, 128.21, 128.7, 133.0, 137.3, 200.7 ppm. Repetition of the foregoing procedure but workup with 1 N DCl in D_2O (98% D) gave **20**, which was ca. 75% monodeuteriated at the C-2 position (diminution of the ^{1}H triplet area at δ = 2.96 ppm by 38%).

(5) Diphenylacetylene (8): The reaction mixture with **8** was stirred at 20–25 °C for 24 h. The original dark purple mixture had by then turned dark brown. Workup with 6 N aqueous HCl (gas evolution) and usual processing gave an organic residue, after solvent removal, that was analyzed directly by ^{1}H and ^{13}C NMR spectroscopy. The residue was composed of (*Z*)-stilbene (**9**, 8%), (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (**10**, 10%), (*Z*)-1,2-diphenyl-1-hexene (**11**, 18%) and (*E*)-1,2-diphenyl-1-hexene (**12**, 64%). The hexenes **11** and **12** could be separated from **9** and **10** by column chromatography on silica gel with elution by hexanes. ^{1}H NMR of (*Z*) isomer (**11**, 18%) ($CDCl_3$): δ = 6.5 (s, C-1), 2.48 (t, C-3), 1.30 (q, C-4), 0.80 (sext, C-5), 0.60 (t, C-6) ppm (key hexane peaks). ^{1}H NMR of (*E*) isomer (**12**, 64%) ($CDCl_3$): δ = 6.73 (s, C-1^1), 2.70 (t, C-3), 1.30 (q, C-4), 0.80 (sext, C-5), 0.60 (t, C-6) ppm (key hexane peaks). The positions of the C-H signals for the (*Z*) and (*E*) isomers are in relative fields (δ = 6.51 and 6.73 ppm) in reasonable agreement for literature values in dioxane (δ = 6.38 and 6.64 ppm).[19]

Reactions of Iron(III) Chloride with 3 mol-equiv. of Benzylmagnesium Chloride: Benzylmagnesium chloride was freshly prepared from benzyl chloride and magnesium turnings in diethyl ether at 0.67 M. To 50 mL of anhydrous diethyl ether under argon was added $FeCl_3$ (97%, 5.0 g, 30.0 mmol) and the mixture stirred and cooled to –78 °C. Then 100 mmol of the benzyl Grignard reagent was added dropwise. The resulting partial solution turned dark brown and almost black as the mixture warmed to 12 °C (stirbar coated with iron). After 24 h, the reaction was quenched with 1 N aqueous HCl, leading to gas evolution. Usual workup led to the detection of only bibenzyl in the organic residue. The foregoing reaction was repeated in that diphenylacetylene (5.34 g, 30 mmol) was added to the $FeCl_3$ in diethyl ether at –78 °C before the benzyl Grignard reagent was introduced. As with the 1:3 reaction of the $FeCl_3$/*n*-butyllithium reactions, this alkyne was to serve as a chemical trapping agent for any carbene formed, in this case the iron(III)–benzylidene **28**. Indeed, hydrolytic workup, column chromatography on silica gel with hexane eluent and ^{1}H NMR analysis showed the presence of bibenzyl (58%), (*Z*)-1,2,3-triphenyl-1-propene (**32**, 17%), 2,3-diphenylindene (**31**, 7%) and (*E*)-1,2,3-triphenyl-1-propene (**33**, 17%). Quantification of the yields was achieved by integrating the area of a single CH_2 signal in each product: (*Z*) isomer (**32**), δ = 3.70 (d, 2 H) ppm; (*E*) isomer (**33**), δ = 4.08 (s, 2 H) ppm; indene (**31**), δ = 3.92 (s, 2 H) ppm. The products **31**, **32** and **33** have been shown to be the typical protolysis products of the corresponding nickel–carbene **35** (vide supra).[12,13]

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[13] Although dark green **35** has not been isolated analytically pure, its ^{13}C NMR spectrum exhibits a sharp peak at δ = 251 ppm, characteristic of nickel(0)–carbenes; furthermore, **35** reacts with diphenylacetylene to produce 1,2,3,4,5-pentaphenylcyclopentadiene.[12a]

[14] Since iron(III) halides and alkyliron(III) compounds are Lewis acids, such derivatives as **6** and **7** can be expected to exist in these THF reaction mixtures as complexes with Lewis bases present, such as **6**·THF and/or **6**·LiCl.

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