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Fluorinated butatrienes

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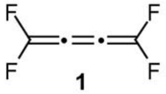
ABSTRACT

Major improvements in the synthesis of 1,1,4,4-tetrafluorobutatriene (**1**) are presented. Despite many attempts to isolate new metal complexes of **1** only an iron complex containing a ligand which is composed of a partially hydrolyzed tetrafluorobutatriene-dimer and carbon monoxide could be isolated and characterized by X-ray crystallography. Certain metal centers and solvents accelerate the decomposition of **1**. First attempts to synthesize 1,1-difluorobutatriene (**2**) are presented which underline the major challenges of a successful synthesis of **2**.

1. Introduction

1,1,4,4-Tetrafluorobutatriene **1** was first prepared by Martin and Sharkey in 1959 [1]. Its chemistry remained almost unexplored due to the compound's extreme instability, it polymerizes even at −85 °C and is said to explode violently on warming to −5 °C or contact with air. Even in inert solution it decomposes within a few hours forming numerous unresolved oligomers. The known chemistry of **1** is limited to a few derivatives also reported by Martin and Sharkey, obtained by addition of bromine and chlorine, and oxidation [1]. Later, Raman- and PE-spectroscopic data were added [2,3] and its structure and experimental charge density were elucidated by high-resolution X-ray diffraction [4]. Recently, the first perfluorobutatriene complexes [IrCp*(PMe$_3$)(C$_4$F$_4$)] [5] and [M-*trans*-(PPh$_3$)$_2$(CO)(2,3-η^2-C$_4$F$_4$)Cl] (M = Rh, Ir) [6] were synthesized by reduction of a *sec.*-perfluorobutyl ligand in the coordination sphere of iridium and from the free butatriene, respectively. Additionally, **1** reacts with dienes forming the product of a Diels-Alder reaction [7].

The only known partially fluorinated butatriene, 1,1-difluorobutatriene **2** was synthesized and spectroscopically characterized by low temperature matrix-isolation experiments by Sander and co-workers [8]. Until recently, none of the other partially fluorinated butatrienes did appear in the literature. Recently, we have studied all partially fluorinated butrienes as well as their enyne isomers by computational chemistry methods [9]. Herein we report on the optimization of the synthesis of tetrafluorobutatriene, its coordination chemistry and first attempts of the synthesis of compound **2**.



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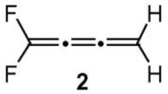

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2. Results and discussion

2.1. Revised synthesis of tetrafluorobutatriene

An improved synthesis of **1** starting from commercially available 1,1-difluoroethene (**3**) is depicted in Scheme 1.

The previously published syntheses of the precursor 2,2-difluoroiodoethene (**5**) for the synthesis of **1** by Lacher and co-workers [10,11] and later by Lentz and co-workers [12] could be improved since both suffered from some disadvantages. The elimination of hydrogen chloride from 1-chloro-2,2-difluoro-2-iodoethylene (**4**) by potassium hydroxide in high boiling mineral oil resulted in high conversion to the precursor **5** but due to separation problems during the fractional condensation, yields remained rather poor. The elimination of hydrogen chloride from **4** by potassium *tert.*-butoxide produces *tert.*-butanol and hence involves the severe problem of separating the product from *tert.*-butanol. Since *tert.*-butanol is a ball-shaped molecule, it passes cooling traps even if they are cooled well beyond its boiling or freezing point due to the high sublimation pressure of such compounds [13,14]. Therefore purification has to be repeated several times which consequently lowers the yield.

It turned out, that the elimination employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2,6-lutidine results in a high

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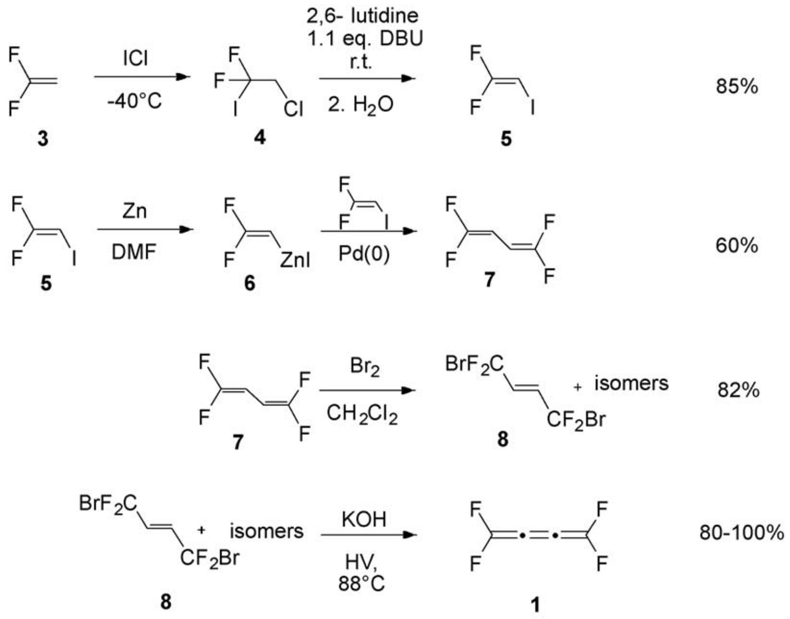


Scheme 1. Improved synthesis of tetrafluorofluorobutatriene (**1**).

conversion rate (Scheme 1, line 1), but large amounts of salt precipitate during the reaction and incorporate substantial amounts of the product, thereby lowering the yield.

This problem can be solved in two different ways. For small scale preparations one can remove solvent and volatiles and use the content which do not pass a −40 °C cooling trap as solvent for another elimination. While yields in the first run are approximately 75%, it increases in every further run to 85–90%. Regarding the limited volatility of 2,6-lutidine this work-up is time consuming. For larger scale preparations the salts are dissolved in water to allow an easier separation of the volatile materials by fractional condensation under vacuum. Finally the volatiles are distilled yielding 85% of analytically pure **5**. The reaction was scaled up to a two-mole scale without any noticeable decrease in yield.

Furthermore it turned out, that careful addition of bromine to **7** is important to obtain good yields of **8**. Compound **8** is stable in air and room temperature but within several weeks the color changes to slightly pink. Nevertheless ^{19}F NMR spectra showed no change of the compound.

The reaction conditions for the syntheses of **1** were optimized as follows: the elimination is performed over hot potassium hydroxide in a U-shaped-glass-pipe under high vacuum. The U-pipe is connected to two cooling traps, −78 °C to collect remaining starting material and water and −196 °C to collect the product. It turned out that:

1st: decrease of the elimination temperature in the U-pipe to 88 °C,
2nd: reduction of the stream of the starting material,
3rd: use of technical potassium hydroxide flakes instead of chemical grade pellets,
4th: use of a thin U-pipe with an inner diameter of below 1 cm, results in reproducible yields of 80–100%.

Up to 2 g (∼8 mmol) of the starting material can be converted until the U-pipe is plugged up by the resulting molten potassium hydroxide/water mixture.

It is very important that the pressure in the system must not exceed 10^{-2} mbar otherwise volatiles are produced that even pass the liquid nitrogen cooled trap, most likely carbon monoxide resulting from further reactions of **1** with potassium hydroxide. This can be caused by a too intense stream of starting material. The use of technical grade potassium hydroxide proved to be useful, presumably for two reasons: at first, the surface texture of the technical potassium hydroxide is more rough compared to chemical grade pallets. Hence the contact surface is increased. Secondly, possible admixtures, e.g. potassium carbonate, could play an important role. Consequential, the U-pipe has to have a small diameter since larger ones result in larger amounts of used potassium hydroxide and the contact surface is further increased. However, an oversized contact surface results in a decrease of the yield.

Summing up, there is a complex equilibrium between contact time, contact surface, type of base and temperature which governs the yield. The conditions mentioned above proved to give reliable an overall yield of 42% of **1**.

Martin and Sharkey stated that tetrafluorobutatriene explodes when heated above its boiling point or in contact with air [1]. We did not observe such an explosion when tetrafluorobutatriene (1 g) was subjected to room temperature under its own vapor pressure. Nevertheless, pure tetrafluorobutatriene **1** polymerizes even at −78 °C and rapidly at room temperature to give a slightly pink to red polymer.

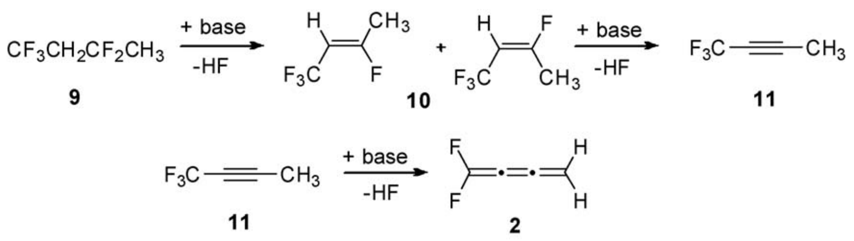
Once prepared, it can only be transferred safely by condensation at reduced pressure and must be stored at −196 °C. This method has so far prevented explosion and polymerization.

2.2. Attempted synthesis of 1,1-difluorobutatriene

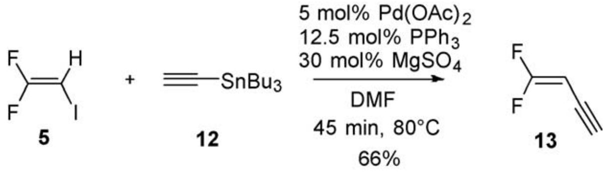
Several potential strategies for the synthesis of 1,1-difluorobutatriene are outlined below. All of them involve dehydrohalogenation, dehalogenation or rearrangement steps.

The potential synthesis of 1,1-difluorobutatriene depicted in Scheme 2 looks especially attractive as it starts from the commercially available hydrofluorocarbon 1,1,1,3,3-pentafluorobutane (**9**) (Solkane® 365 mfc).

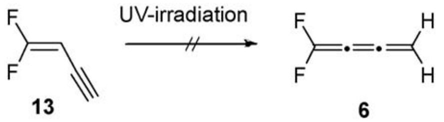
Although the but-2-enes **10** and the alkyne **11** could be detected in the reaction mixture on treatment of **9** with various bases like



Scheme 2. Attempted synthesis of 1,1-difluorobutatriene (**2**) by subsequent elimination of hydrogen fluoride from 1,1,1,3,3-pentafluorobutane (**9**).



Scheme 3. Palladium-catalyzed synthesis of 1,1-difluorobut-1-en-3-yne (**13**).



Scheme 4. Attempted rearrangement of 1,1-difluorobut-1-en-3-yne (**13**).

potassium hydroxide, butyl lithium, LDA or potassium *t*-butoxide by ^{19}F NMR spectroscopy it turned out impossible to isolate **11** in preparative amounts. In all cases a complex mixture of **9**, **10** and **11** is obtained when stochiometric amounts of butyl lithium were used. Using an excess of butyl lithium results in complete decomposition without any hint for the formation of **2**.

Sander et al. reported the synthesis of 1,1-difluorobutatriene (**2**) by laser induced (193 nm) rearrangement of 1,1-difluorobuta-1-en-3-yne (**13**) within an argon matrix. The only other report on **13** is a patent by E.I. Du Pont de Nemours & Co. [15]. They claim its synthesis by pyrolysis of 1-ethynyl-2,2,3,3-tetrafluorocyclobutane and the use of its group I and II metal salts as an additive to fuels for internal-combustion engines and as bactericides.

A new synthesis of **13** was developed based on palladium-catalyzed Stille cross-coupling of ethynyl-tri-*n*-butylstannane (**12**) with 1,1-difluoro-2-iodo-ethene **5** (Scheme 3).The crude product was purified by fractional condensation to give >95% pure **13** according to ^{19}F, ^{1}H and ^{13}C NMR spectra. Addition of magnesium sulfate to the reaction mixture proved to be useful, under identical conditions a run without magnesium sulfate yielded only 41% [16].

An UV–vis spectrum of the enyne (**13**) showed bands at 214, 225 and 230 nm and the enyne was therefore subjected to gas phase UV-irradiation but no rearrangement was observed after 24 h of irradiation (Scheme 4).

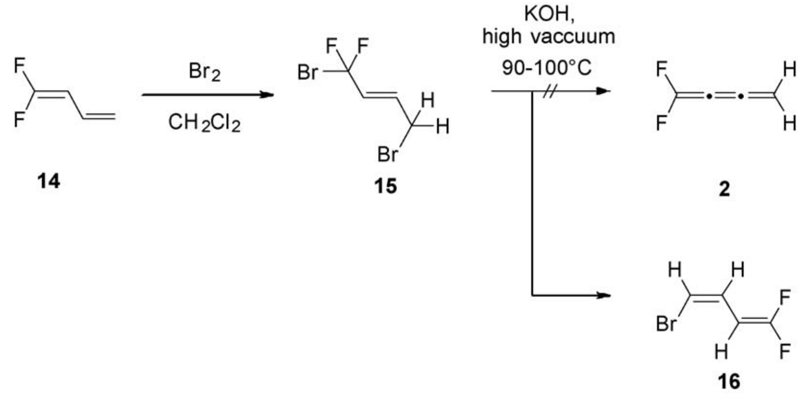
The experiences gained from the handling and synthesis of tetrafluorobutatriene (**1**) advise a similar synthetic strategy for the synthesis of 1,1-difluorobutatriene (**2**): gas phase hydrogen halide elimination from a suitable precursor and immediate cooling to −196 °C.

A reasonable starting point was a synthetic route analogous to the synthesis of **1** according to Scheme 5. However, the dehydrobromination of **15** gives Z-1-bromo-4,4-difluorobutadiene (**16**) but does not proceed further to yield **2**.

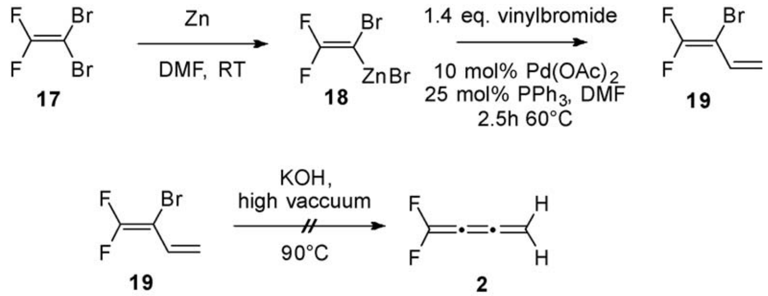
It seemed necessary to use a brominated diene (**19**) which is only capable of eliminating hydrogen bromide in the desired modality (Scheme 6). Elimination of hydrogen bromide from **19** could only yield **2**. After numerous unsuccessful attempts, it turned out that only Negishi cross-coupling of 1,1-dibromo-2,2-difluoroethene (**17**) with vinylbromide affords isolable yields of the desired diene **19** (Scheme 6).

The synthesis of **18** as well as the synthesis of α-halo-β,β-difluorovinylzinc compounds has previously been reported by Burton [17,18]. It turned out that elimination of hydrogen bromide from **19** over hot potassium hydroxide under high vacuum conditions is not possible. The diene **19** passes the reaction zone unchanged. Whether the failure is due to thermodynamic or kinetic effects remains still unclear.

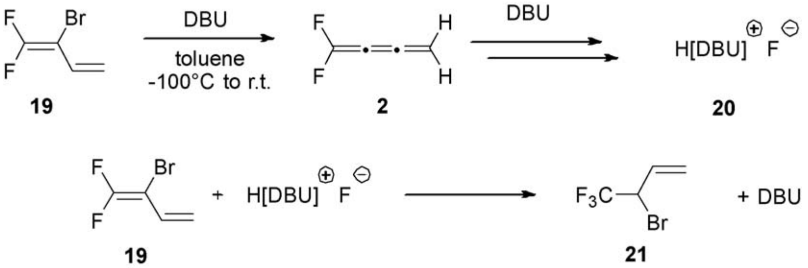
Since the elimination of hydrogen bromide over hot potassium hydroxide proved unsuccessful, an alternative elimination from **19** in solution by a strong hindered base (DBU) was examined (Scheme 7). The reaction was monitored by ^{19}F NMR spectroscopy. A new signal at −99.5 ppm was detected close to that of tetrafluorobutatriene **1**. However, this resonance vanishes within



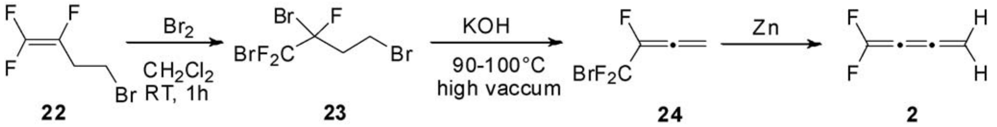
Scheme 5. Proposed synthesis of 1,1-difluorobutatriene by a bromination/double dehydrobromination sequence and observed reaction.



Scheme 6. Palladium-catalyzed synthesis of 2-bromo-1,1-difluorobuta-1,3-diene (**19**) and attempted dehydrobromination.



Scheme 7. Attempted synthesis of 1,1-difluorobutatriene by elimination of hydrogen bromide from **19** by treatment with DBU and unexpected formation of (**21**).



Scheme 8. Proposed mechanism for the synthesis of 1,1-difluorobutatriene by bromination/dehydrobromination of 4-bromo-1,1,2-trifluorobut-1-ene and subsequent elimination of zinc(II)halide.

an hour when the reaction mixture is subjected to room temperature.

Unfortunately, even at −50 °C the predominant signal of 3-bromo-4,4,4-trifluorobut-1-ene **21** is rapidly formed. The elimination may take place and triene **2** is formed but further reaction with DBU leads to defluorination. Since the diene **19** is the only fluorine source in the reaction, it is most likely that DBU-hydrogen fluoride is formed intermediately which then subsequently adds hydrogen fluoride to the remaining diene **19**. This finding is comparable to the hydrofluorination of alkenes by Olah's reagent (x(HF) • pyridine) [19]. Butene **21** was isolated from the reaction mixture by fractional condensation and identified by its ^{19}F, ^{1}H and ^{13}C NMR spectra.

Finally, 1,1,2-trifluoro-4-bromo-but-1-ene **22** was brominated using bromine in dichloromethane. The reaction product **23** was isolated by fractional condensation in excellent yield (95%) and high purity (>99%) (Scheme 8).

The tribromo compound **23** was then subjected to high vacuum elimination over hot potassium hydroxide. NMR spectroscopy of the product revealed that only one elimination of hydrogen bromide took place forming butene **25** and not the buta-1,2-diene **24** (Schemes 8 and 9).

2.3. Attempts to synthesize metal complexes of tetrafluorobutatriene

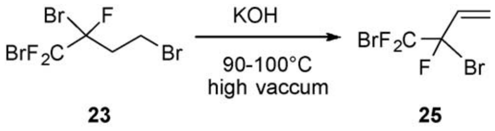
Photochemical displacement of a carbonyl ligand by THF and reaction with the cumulene, a successful approach in the synthesis of fluoroallene complexes [20], gave no evidence of the formation of a tetrafluorobutatriene complex.

Neither reaction with tetracarbonyl(η^5-cyclopentadienyl)vanadium (**26**) [21], tricarbonyl(η^5-cyclopenta-dienyl)manganese (**27**) [22], tricarbonyl(η^6-benzene)chromium (**28**) [23], tricarbonyl(η^6-mesitylene)chromium (**29**) [24], dicarbonyl(η^5-cyclopentadienyl)cobalt (**30**) [25] nor the chromo ethylene complex **31** [26] gave successful reactions.

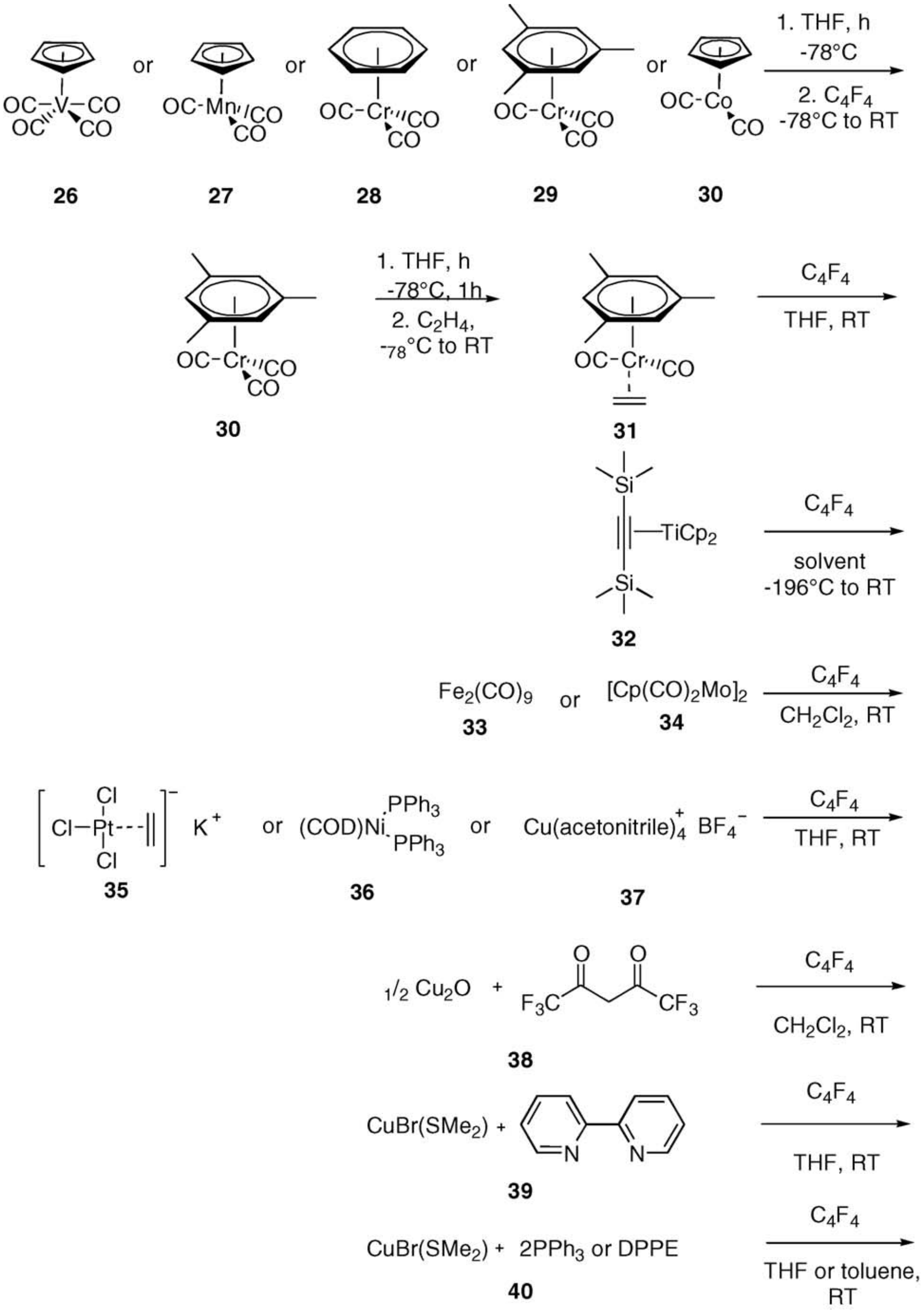
According to Rosenthal [27], the bis(trimethylsilyl)acetylene ligand in the titanium complex (**32**) is easily removable for example by substituted butatrienes. Similar reactions were described by Suzuki using the 'Negishi reagent' dibutyldicyclopentadienylzirconium [28]. A reaction with **1** was not observed.

Reactions based on the reactivity of metal–metal bonds in enneacarbonyldiiron (**33**), and bis[(dicarbonyl)(η^5-cyclopentadienyl)molybdenum] (**34**) successfully yield difluoroallene complexes[29] but formation of tetrafluorobutatriene complexes was not observed (Scheme 10).

Reactions with complexes containing labile ligands like Zeise's salt (**35**) [30], bis(triphenylphosphine)(cyclooctadiene)nickel (**36**) [31] and tetraacetonitrilecopper(I)-tetrafluoroborate (**37**) [32] also did not yield isolable tetrafluorobutatriene complexes, too. Instead accelerated polymerization was observed for **35** and **36**.



Scheme 9. Attempted synthesis of 1,1-difluorobutatriene by multiple dehydrobromination of **23**.



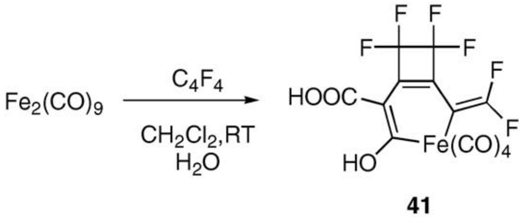
Scheme 10. Attempted synthesis of tetrafluorobutatriene metal complexes.

Finally, the copper(I) complexes (**38**)–(**40**) were examined (Scheme 8) [32–34]. Tetrafluorobutatriene copper complex formation was not observed.

Several metals turned out to accelerate the polymerization. This finding is significant for nickel, platinum and titanium. Furthermore, the stability of tetrafluorobuatriene **1** in different solvents increases in the row pentane < diethylether ≈ THF < CH_2Cl_2 ≈ $CHCl_3$. High dilution conditions stabilize tetrafluorobutatriene **1** but have a decelerating effect on the reaction rate.

2.4. An unexpected iron complex of tetrafluorobutatriene

Unlike 1,1-difluoroallene and tetrafluoroallene which form η^2-complexes by reactions with several transition metal complexes [35] similar reactions with tetrafluorobutatriene were unsuccessful in most cases. The only tetrafluorobutatriene complexes obtained directly from the triene are $[Ir(\eta^2\text{-}C_4F_4)(CO)(PPh_3)_2Cl]$ and the analogous rhodium compound, as previously mentioned. In one of the many attempts to react tetrafluorobutatriene with enneacarbonyldiiron a few colorless crystals of an unexpected product (**41**) were obtained (Scheme 11).



Scheme 11. Synthesis of iron complex **42**.

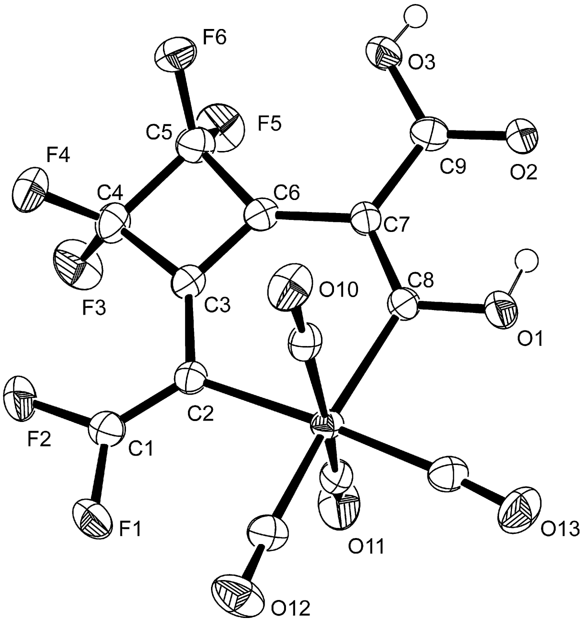


Fig. 1. Molecular structure (ORTEP [36]) of compound 41.

The crystal and molecular structure of **41** was elucidated by X-ray crystallography (Fig. 1). The iron atom is almost octahedrally coordinated by two carbonyl ligands in the trans positions and two other carbonyl ligands in cis position to the two carbon atoms of the ferracyclohexadiene-ring. The bond angle C10–Fe1–C11 of 163.97(12)° of the carbonyl ligands trans to each other deviates significantly from linearity. All carbon atoms within the ring are sp^2-hybridized (angles range from 116.65(12)° to 130.4(2)°) and the ring itself is almost planar. The C2–Fe–C8 bond angle of 95.50(11)° is the smallest in the ferracyclohexadiene-ring. The iron carbon bonds Fe–C8 (2.029(3) Å) and Fe–C2 (2.054(3) Å) are slightly different and longer than the distances to the carbonyl ligands.

As expected for solid carbon acids two molecules are interconnected by hydrogen bridging bonds.

The ^{19}F NMR and IR-spectra of **41** are in accordance with the molecular structure obtained by X-ray diffraction. Despite many further attempts the synthesis of **41** remained irreproducible.

One can only speculate about the mechanism of the formation of **41**. There exist at least two principally different pathways. First, dimerization of tetrafluorobutatriene, coordination of the dimer, CO insertion and partial hydrolysis. Second, iron promoted dimerization forming a metallacycle, formation of the four membered ring, CO insertion and partial hydrolysis. As already found by Wilkinson, tetrafluoroethene reacts with iron carbonyls forming a ferracyclopentane by oxidative addition [37]. Similar metallacycles have been obtained for phosphine, bipyridyl and cyclooctadiene complexes of nickel [38]. To our knowledge, a CO insertion into the five-membered fluorinated metallacycle has not been observed up to now. In contrast, CO insertion into hydrocarbons plays an important role in industrial processes (Monsato process, hydroformylation) and occurs even in non-fluorinated butatriene complexes [39]. $Fe(CO)_4(CO–CF_2–CF_2–CF_2–CO)$ has been synthesized from perfluoroglutaryl chloride and structurally characterized by X-ray diffraction [40]. The subsequent hydrolysis of one of the metal-bound fluorocarbyl groups is well known going back to work by Kemmitt [41] in the 1960s and has been recently reviewed by Hughes [42]. Recently, a partially hydrolyzed trimer of tetrafluoroallene as well as a manganese complex of the tetrafluoroallene dimer were structurally characterized [43].

3. Conclusion

The instability of tetrafluorobutatriene as well as the acceleration of its decomposition by certain metal centers makes its chemistry challenging. Despite many attempts only an accidentally synthesized iron complex could be isolated. Several possible strategies for the successful synthesis of 1,1-difluorobutatrienes were attempted experimentally, but none of them yielded isolable amounts of this species. Further studies are ongoing in our laboratory.

4. Experimental

4.1. General techniques

All manipulations of air and moisture sensitive compounds were performed on a standard vacuum line in flame dried flasks under an atmosphere of argon. The argon, purification grade 4.8, was provided by LINDE. Solvents were distilled under argon from sodium (toluene, pentane, hexane, and benzene), sodium/benzophenone (THF, DME, diethyl ether, and *tert.*-butylmethyl ether) or phosphorous pentoxide (DMF, dichloromethane, chloroform, tetrachloromethane, and acetonitrile). Solvents were stored over sodium–potassium alloy (ethers and hydrocarbons) or 3 Å molecular sieve (DMF, acetonitrile and chlorohydrocarbons) in flasks with Normag or Young plug valve and transferred to the reaction vessels via standard vacuum techniques (condensation) or Schlenk technique. Air-sensitive compounds were stored and weighted in a glovebox (MBraun Labmaster sp). Unless otherwise noted all manipulations were carried out using standard Schlenk techniques in an argon counterflow to exclude moisture and air. Cooling of reaction mixtures up to −125 °C was performed by ethanol/liquid nitrogen mixtures. Lower temperatures up to −160 °C were obtained by *iso*-pentane/liquid nitrogen mixtures. Unless otherwise noted all reaction temperatures are internal temperatures, especially involving exothermic reactions at low temperatures.

Commercially available chemicals were used without further purification. NMR measurements were carried out on a JEOL Lambda 400 spectrometer at 20 °C (if not indicated differently). Temperatures below room temperature were reached by evaporation of liquid nitrogen. Temperature sensitive compounds were transferred into the precooled spectrometer without interruption of the cold chain. Air and moisture sensitive compounds were measured in sealed NMR tubes (Young) or flame sealed 4-mm-Duran-glass-tubes. Chemical shifts δ are given by definition as dimensionless number. The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Spectra were referenced with internal standards: for ^{1}H and ^{13}C NMR (solvent signal) and external standards for ^{19}F and ^{119}Sn NMR ($CFCl_3$ and tetramethyltin). Measurement frequencies are 399.65 MHz (^{1}H), 100.40 MHz (^{13}C), 376.00 MHz (^{19}F) and 148.95 MHz (^{119}Sn).

Crystal structure data were collected on a Bruker SMART-CCD-1000-TM diffractometer with Mo Kα-radiation at −100 °C. A suitable crystal was selected on an installation described in the literature using a microscope, mounted onto a glass fiber using silicon grease and transferred into the cold gas stream of the diffractometer [44]. Empirical absorption correction was done with SADABS [45]. Structure solution and refinement was done using the least square refinement method implemented in the SHELX program suite [46]. Pictures were created using ORTEP [36].

4.2. General working procedures

4.2.1. 1,1-Difluoro-2-iodoethylene (5)

100 g (0.6 mol) iodinemonochloride (ICl) in a flame dried 2-L flask with a Normag type teflon plug valve and a magnetic stir bar were cooled to −196 °C and evacuated (3 times). The reaction vessel and the difluoroethylene gas flask were connected to the vacuum line. At 0 °C (ice bath) 40 g (0.62 mol) difluoroethylene was added in portions over the vacuum line, monitored by a vacuum gauge. Then 300 mL of 2,6-lutidine were added at 0 °C followed by the fast addition of 110 g (0.72 mol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The valve at the reaction was closed and the mixture slowly warmed to room temperature and stirred overnight. All volatiles were condensed into a −196 °C cooling trap. 3 portions of 50 mL of water were added to the reaction mixture and the mixture was stirred for 5 min. Again all volatiles were condensed into the trap. 1,1-difluoro-2-iodoethylene was distilled off (b.p. 35 °C) to yield 97 g (85%) of the pure product (purity > 99%). A scale up of the reaction to 2 mol iodine monochloride gave an equal yield.

^{1}H NMR ($CDCl_3$, 20 °C): $\delta = 4.82$ (dd). ^{19}F NMR ($CDCL_3$, 20 °C): $\delta = -71.36$ (dd); -75.79 (dd). Full spectroscopic data see Ref. [11].

4.2.2. 1,1,4,4-Tetrafluorobuta-1,3-diene (7)

The previously published method was modified as follows. Zinc was carefully activated by treatment with dilute hydrogen chloride and subsequently washed with water, ethanol and acetone and finally dried in high vacuum. Only the finest powder was employed in the following synthesis. 1,1-Difluoro-2-iodoethylene (13 g, 68.45 mmol) was added dropwise to activated zinc powder (8 g) in DMF (50 mL) at room temperature. An exothermic reaction occurs. ^{19}F NMR measurement revealed complete conversion to the zinc compound [47]. The zinc reagent was transferred to a second flask containing $[Pd(PPh_3)_4]$ (2 g, 1.7 mmol, 2.5 mol%) and 1,1-difluoro-2-iodo ethylene (13 g, 68.45 mmol) via a small diameter teflon tube. The reaction temperature was maintained at 75 °C for 4 h. Meanwhile the product was collected as a colorless liquid in a trap kept at −78 °C which was connected to the reflux condenser. Fractional condensation under vacuum (10^{-3} mbar) yielded 5.2 g (61%) in the trap kept at −120 °C.

^{1}H NMR ($CDCl_3$, 20 °C): $\delta = 4.52$ (m, 2H). ^{19}F NMR ($CDCL_3$, 20 °C): $\delta = -86.77$ (m); -88.09 (m). Full spectroscopic data see Ref. [4].

4.2.3. 1,4-Dibromo-1,1,4,4-tetrafluorobuta-1,3-diene (8)

The previously published method was modified as follows. Compound (**7**) (5.2 g, 40 mmol) was condensed onto bromine (6.4 g, 42 mmol) in CH_2Cl_2 (10 mL) in a 100 mL glass flask. The reaction mixture was rapidly warmed to room temperature and stirred for 5 h at ambient temperature. 5 mL of sodium thiosulfate saturated water was added and the mixtures were stirred for 5 min. The layers were separated, the water phase extracted 3 times with 2 mL of dichloromethane. Fractional condensation of the combined organic phases under vacuum yielded (**8**) (9.87 g, 82%) as a colorless liquid in the trap kept at −60 °C.

^{1}H NMR ($CDCL_3$, 20 °C): $\delta = 6.33$ (m). ^{19}F NMR ($CDCL_3$, 20 °C): $\delta = -50.30$ (m). Full spectroscopic data see Ref. [11].

4.2.4. 1,1,4,4-Tetrafluorobuta-1,2,3-triene (1)—general procedure for elimination in the gas phase over hot potassium hydroxide

Compound (**8**) (1 g, 3.5 mmol) was passed over technical grade KOH which was filled into a U-shaped tube with a diameter of no more than 1 cm and heated to 88 °C by evaporation under vacuum (10^{-3} mbar). The volatile materials were collected in traps kept at −78 °C (water) and −196 °C (**3**). No repetition was necessary. A yield of up to 100% was determined by weighting in a Young-valve tube.

^{19}F NMR (CD_2Cl_2, 193 K): $\delta = 96.1$ (s). Full spectroscopic data see Ref. [11].

4.2.5. Attempted synthesis of 1,1-difluorobutatriene (2) by multiple hydrogen fluoride elimination from 1,1,1,3,3-pentafluorobutane (25)

10 mmol (1.5 g) 1,1,1,3,3-pentafluorobutane was diluted with the appropriate solvent (see Table 2.4.2) in a flame dried Young-valve 50-mL-flask. With the exception of butyllithium and LDA (addition temperature, reaction time see Table) all bases were added at room temperature. The reaction was monitored by NMR spectroscopy (see Table for results).

Physical data of observed intermediates:

1,1,1,3,3-Pentafluorobutane (**9**): ^{19}F NMR ($CDCl_3$, 20 °C): $\delta = -64.15$ (3F, m), -88.95 (2F, m).
1,1,1,3-Tetrafluorobut-2-ene (**10**): ^{19}F NMR ($CDCl_3$, 20 °C): isomer 1: $\delta = -59.16$ (3F, m), -83.2 (1F, m). Isomer 2: $\delta = -57.84$ (3F, m), -83.3 (1F, m).
1,1,1-Trifluorobut-2-yne (**11**): ^{19}F NMR ($CDCl_3$, 20 °C): $\delta = -50.41$ (3F, q, $^{5}J(F–H) = 4$ Hz). ^{1}H NMR ($CDCl_3$, 20 °C): $\delta = 1.95$ (3H, q, $^{5}J(H–F) = 4$ Hz).

4.2.6. Synthesis of 1,1-difluorobuta-1-en-3-yne (13)

In a flame dried Young-valve 50-mL-flask 7.56 g n-butylstannylacetylene (24 mmol, 1.04 eq.) and 4.37 g 1,1-difluoro-2-iodoethylene (23 mmol) were added to 250 mg palladium(II)acetate (5 mol%), 750 mg triphenylphosphine (12.5 mol%) and 1 g magnesium sulfate in 20 mL DMF. The reaction vessel was heated to 80 °C (bath-temperature) for 45 min. The color of the reaction mixture changes to black during heating. The reaction mixture was subjected to fractional condensation in high vacuum (10^{-3} mbar) over a −78 °C cooling trap. The product, 1.4 g (66% yield) of a colorless gas, was collected in a −196 °C cooling trap and stored in a Young-valve flask in the fridge at 4 °C.

^{19}F NMR ($CDCl_3$, 20 °C): $\delta = -76.53$ (1F, d, $^{3}J(F–H) = 22.8$ Hz), -81.70 (1F, s) no geminal F–F coupling observable. ^{1}H NMR ($CDCl_3$, 20 °C): $\delta = 5.22$ (1H, dm, $^{3}J(H–F) = 22.8$ Hz), all other coupling constants could not be resolved, 3.58 (1H, m). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): $\delta = 163.9$ (1C, dd, CF_2, $^{2}J(C–F) = 293$ Hz, 300 Hz), 81.2 (1C, dd, J(C–F) = 4 Hz, 9 Hz), 71.9 (1C, dd, J(C–F) = 4 Hz, 12 Hz), 64.4 (1C, J(C–F) = 19.5 Hz, 43 Hz).

4.2.7. Attempted rearrangement of 1,1-difluorobuta-1-en-3-yne (13)

1 mmol (ca. 100 mg) **13** was condensed into a Normag-valve 2-L-flask and irradiated at room temperature for 4 h. All volatiles were condensed onto $CDCl_3$ in a 4-mm-glass-tube. ^{19}F NMR revealed only starting material.

4.2.8. Synthesis of E-1,4-dibromo-1,1-difluoro-2-butene (15)

A flame dried Young-valve 25-mL-flask, equipped with a magnetic stir bar, was charged with 2.63 g (29 mmol) 1,1-difluorobutadiene. Bromine (31 mmol, 4.96 g) was added in small portions by condensation. Distillation via a spinning band column at reduced pressure of 12 mbar yielded 4.08 g (56%) **15** in 97% purity.

^{19}F NMR ($CDCl_3$, 20 °C): $\delta = -46.83$ (2F, CF_2Br–, dd, $^{3}J(F–F) = 9.7$ Hz, $^{4}J(F–H) = 1.9$ Hz). ^{1}H NMR ($CDCl_3$, 20 °C): $\delta = 6.33$ (1H, $H_2BrC–CH$– dtt, $^{3}J(H–trans–H) = 15.2$ Hz, $^{3}J(H–CH_2Br) = 7.2$ Hz, $^{4}J(H–F) = 1.9$ Hz), 6.10 (^{1}H, $F_2BrC–CH{=}$, dtt, $^{3}J(H–trans–H) = 15.2$ Hz, $^{3}J(H–F) = 9.7$ Hz, $^{4}J(H–CH_2Br) = 1.3$ Hz), 3.94 (2H, dd, $^{3}J(H–H) = 7.2$ Hz, $^{4}J(H–H) = 1.3$ Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20 °C): $\delta = 131.0$ (1C, t, CF_2, $^{1}J(C–F) = 7.5$ Hz), 129.7 (1C, t, $^{2}J(C–F) = 24.4$ Hz), 115.7 (1C, t, $^{1}J(C–F) = 301$ Hz), 28.0 (1C, s).

4.2.9. Attempted elimination of hydrogen bromide from E-1,4-dibromo-1,1-difluoro-2-butene (15)

The attempted elimination was performed according to the general procedure described in Section 4.2.4. A temperature of 90 °C was employed. The product was identified by NMR data as 1-bromo-4,4-difluorobutadiene (**16**).

^{19}F NMR (CDCl$_3$, 20 °C): δ = −81.82 (1F, dddd, ^{3}J(F-*trans*-H) = 24.3 Hz, ^{2}J(F–F) = 16.7 Hz, ^{4}J(F–H) = 1.7 Hz, ^{5}J(F–F) = 1.1Hz), −83.67 (1F, dddd, ^{2}J(F–F) = 16.7 Hz, ^{3}J(F-cis-H) = 1.4 Hz, ^{4}J(F–H) = 1.1 Hz, ^{5}J(F–F) = 1.4Hz). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 6.59 (1H, –*H*C═CHBr, dddd, ^{3}J(H–H) = 10.8 Hz, ^{3}J(H-cis-H) = 7.4 Hz, ^{4}J(H–F) = 1.4 Hz, ^{4}J(H–F) = 1.1 Hz), 6.17 (1H, ═C*H*Br, dddd, ^{3}J(H-cis-H) = 7.4 Hz, ^{4}J(H–H) = 1.2 Hz, ^{5}J(H–F) = 1.4 Hz, ^{5}J(H–F) = 1.1 Hz), 5.38 (1H, F$_2$C═C*H*, dddd, ^{3}J(H-*trans*-F) = 24.3 Hz, ^{3}J(H-cis-F) = 1.4 Hz, ^{3}J(H–H) = 10.8 Hz, ^{4}J(H–H) = 1.2 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 158.0 (1C, dd, *C*F$_2$═, ^{1}J(C–F) = 300 Hz, 293 Hz), 122.6 (1C, dd, ^{4}J(C–F) = 5.4 Hz, 2.1 Hz), 108.3 (1C, dd, ^{3}J(C–F) = 12.0 Hz, 3.7 Hz), 80.0 (1C, dd, ^{2}J(H–H) = 30.6 Hz, 15.3 Hz).

4.2.10. 2-Bromo-1,1-difluorobuta-1,3-diene (19)

In a flame dried 50-mL-Schlenk flask, equipped with a magnetic stir bar, were added 2.2 g (10 mmol) 1,1-dibromo-2,2-difluoroethylene, 654 mg activated zinc dust (finest powder) and 30 mL DMF. A mild exothermic reaction occurred. The solution was stirred overnight. The solution was then transferred via a teflon pipe to another 50-mL-Schlenk flask, equipped with a magnetic stir bar and 225 mg palladium(II)acetate and 655 mg triphenylphosphine (25 mol%).The reaction mixture was frozen in liquid nitrogen and degassed. 1.5 g vinylbromide which was synthesized according to literature methods were condensed onto the reaction mixture. The reaction mixture was heated to 60 °C (bath-temperature) for 2.5 h. Afterwards the mixture was subjected to fractional condensation over cooling traps (−40 °C, −100 °C and −196 °C). The product was collected in the −100 °C trap (1.52 g, 80% purity). The calculated yield was 72%.

^{19}F NMR (CDCl$_3$, 20 °C): δ = −81.03 (1F, dddd, ^{3}J(F–F) = 23.9 Hz, ^{4}J(F–H) = 1.6 Hz, ^{5}J(F–H) = 2.1 Hz, ^{5}J(F–H) = unresolved), −84.23 (1F, dddd, ^{3}J(F–F) = 23.9 Hz, ^{4}J(F–H) = 2.4 Hz, ^{5}J(F–H) = 1.8 Hz, ^{5}J(F–H) = 0.8 Hz). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 6.44 (1H, dddd, ^{3}J(H–H) = 16.3 Hz, ^{3}J(H–H) = 10.3 Hz, ^{4}J(H–F) = 2.4 Hz, ^{4}J(H–F) = 1.6 Hz, C*H*═), 5.51 (1H, ddd, ^{3}J(H–H) = 16.3 Hz, ^{5}J(H–F) = 0.8 Hz, ^{2}J(H–H) = 0.9 Hz, ═C*H*$_2$, *trans*-H), 5.34 (1H, dddd, ^{3}J(H–H) = 10.3 Hz, ^{5}J(H–F) = 2.1 Hz, ^{5}J(H–F) = 1.8 Hz, ^{2}J(H–H) = 0.9 Hz, ═C*H*$_2$, cis H). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 154.8 (1C, dd, *C*F2, ^{1}J(C–F) = 292 Hz, 288 Hz), 126.1 (1C, s, H$_2$*C*═), 119.4 (1C, dd, J(C–F) = 11.6 Hz, 3.5 Hz), 83.0 (1C, J(C–F) = 32 Hz, 24 Hz, *C*Br).

4.2.11. Attempted elimination of hydrogen bromide from 2-bromo-1,1-difluorobuta-1,3-diene (19)

Attempt 1: The attempted elimination was performed according to the general procedure described in Section 4.2.4. A temperature of 90 °C was employed. According to ^{19}F NMR data the starting compound **19** was recovered unchanged.

Attempt 2: A flame dried 4-mm-Duran-glass-tube was charged under argon with 0.05 mL (0.3 mmol) DBU and 0.25 mL toluene-d^{8}. The tube was frozen in liquid nitrogen and degassed. Approximately 50 mg of diene **19** were condensed into the tube. The tube was flame sealed and unfreezed at −80 °C. A variable temperature NMR study was performed (−80 °C up to +10 °C). Predominantly compound **21** is formed, a small signal in the low temperature ^{19}F NMR spectra is observable at −99.5 ppm which might result from the formation of **2**.

Physical data for 3-bromo-4,4,4-trifluorobut-1-ene **21**:

^{19}F NMR (CDCl$_3$, 20 °C): δ = −72.75 (3F, d, ^{3}J(F–H) = 7.1 Hz). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 5.53 (1H, m) 4.80 (2H, m), 3.84 (1H, m). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 129.5 (1C, q, *C*F$_3$, ^{1}J(C–F) = 284 Hz); 129.5 (1C, q, *C*F$_3$, ^{3}J(C–F) = 2 Hz), 125.0 (1C, s), 122.6 (1C, s) 46.50 (1C, q, ^{2}J(C–F) = 34 Hz).

4.2.12. Synthesis of 1,2,4-tribromo-1,1,2-trifluorobutane (23)

In a flame dried 25-mL-Schlenk flask bromine (1.6 g, 10 mmol) was added dropwise at room temperature to a stirred solution of 1.89 g (10 mmol) 4-bromo-1,1,2-trifluorobut-1-ene in 10 mL dichloromethane. The solution was stirred for 1 h. Fractional condensation in high vacuum (10^{-3} mbar) yielded 3.3 g (95%) (**23**) in >99% purity in the cooling trap kept at −30 °C.

^{19}F NMR (CDCl$_3$, 17 °C): δ = −59.00 (1F, m, C*F*$_2$Br), −117.54 (1F, m, C*F*Br). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 3.65 (1H, m, C*H*$_2$Br), 3.55 (1H, m, C*H*$_2$Br), 2.93 (1H, m, C*H*$_2$), 2.80 (1H, m, C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 119.05 (1C, ddd, *C*F$_2$Br, ^{1}J(C–F) = 310 Hz, 312 Hz, ^{2}J(C–F) = 33 Hz), 104.90 (1C, ddd, *C*FBr, ^{1}J(C–F) = 266 Hz, ^{2}J(C–F) = 31 Hz, 28 Hz), 41.70 (1C, d, *C*H$_2$, J(C–F) = 20 Hz), 23.90 (1C, m, *C*H$_2$Br).

4.2.13. Attempted synthesis of 4-bromo-3,4,4-trifluorobuta-1,2-diene (24)

Attempt 1: The attempted elimination was performed according to the general procedure described in Section 4.2.4. A temperature of 90 °C was employed. According to ^{19}F, ^{1}H and ^{13}C NMR data 3,4-dibromo-3,4,4-trifluorobut-1-ene (**25**) is formed by a single hydrogen bromide elimination.

Physical data for 3,4-dibromo-3,4,4-trifluorobut-1-ene (**25**):

^{19}F NMR (CDCl$_3$, 17 °C): δ = −59.2 (1F, m, C*F*$_2$Br), −125.35 (1F, m, C*F*Br). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 3.65 (1H, m, C*H*$_2$Br), 3.55 (1H, m, C*H*$_2$Br), 2.93 (1H, m, C*H*$_2$), 2.80 (1H, m, C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 131.45 (1C, d, *C*H═, ^{2}J(C–F) = 18 Hz), 121.00 (d, ═CH$_2$, ^{3}J(C–F) = 10 Hz), 118.50 (1C, ddd, *C*F$_2$Br, ^{1}J(C–F) = 314 Hz, 310 Hz, ^{2}J(C–F) = 35 Hz), 104.90 (1C, ddd, *C*FBr, ^{1}J(C–F) = 266 Hz, ^{2}J(C–F) = 32 Hz, 29 Hz), 41.70 (1C, d, *C*H$_2$, J(C–F) = 20 Hz), 23.90 (1C, m, *C*H$_2$Br).

4.2.14. General procedure for the generation of metal–THF complexes of 26–30 and metal–ethene complex 31 and attempted synthesis of tetrafluorobutatriene complexes thereof

A photoreactor with water-cooled Pyrex-light, circulation pipe and magnetic stir bar was charged with 0.25 mmol (1 eq.) of the metal complex. The reactor was evacuated for several minutes and afterwards frozen in liquid nitrogen. 50–100 mL pentane and 5–10 mL THF were condensed into the reactor (depending on the size of the reactor). The solvent was degassed again by melting/freezing. The solution was irradiated at −78 °C with a mercury-high-pressure light (Philips HPK-125) for 1 h.

The reaction mixture was frozen in liquid nitrogen and 0.5 mmol tetrafluorobutatriene (A) or 1,1-difluorobut-1-en-3-yne (B) or ethylene (C) were condensed into the reactor. The solution was warmed to room temperature overnight. The solution was filtered under inert condition over a G4-frit and the solvent was removed in high vacuum (for A and B). NMR spectra of the residue revealed no fluorine containing complex.

The solution of C was frozen in liquid nitrogen again and 0.5 mmol tetrafluorobutatriene were condensed into the reactor. The solution was stirred overnight. After a work-up similar to A and B no evidence for the formation of a fluorine containing species was found by ^{19}F NMR, too.

4.2.15. Attempted synthesis of a tetrafluorobutatriene complex of 32

In a flame dried 10-mL-Normag-valve flask, equipped with a magnetic stir bar, were added 0.1 mmol of titanium complex **32** and 5 mL of solvent (either toluene, THF, diethylether, *tert.*-butylmethylether, 1,2-dimethoxyethane, acetonitrile, dichloromethane, chloroform or pentane). The solution was frozen in liquid nitrogen and degassed. 0.25 mmol tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed very slowly to room temperature. Already below −80 °C the solution turned black. ^{19}F NMR spectra showed no evidence for the formation of a fluorine containing titanium complex. A run employing toluene in a Normag-NMR-tube was monitored starting from −100 °C. Nevertheless no evidence for a fluorine containing titanium species was found either.

4.2.16. General procedure for attempted synthesis of a tetrafluorobutatriene complexes of 33–35, 37

In a flame dried 25-mL-Schlenk flask, equipped with a magnetic stir bar, was added 0.1 mmol of the metal complex and 10 mL of solvent (please see Scheme 2.6.4 and 2.6.5 for details). The reaction mixture was frozen in liquid nitrogen and degassed. 0.25 mmol of tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed to −30 °C and argon was added to the vessel for pressure compensation. The reaction mixture was stirred overnight at room temperature. After removal of all volatiles in high vacuum the residue was dissolved in dried d^8-toluene or d^8-THF. ^{19}F NMR spectra showed no evidence for the formation of a fluorine containing complex.

4.2.17. General procedure for attempted synthesis tetrafluorobutatriene complexes of 36 *and* 38–40

In a flame dried 25-mL-Schlenk flask, equipped with a magnetic stir bar, was added:

(**36**) 0.1 mmol dicyclooctadienenickel(0) and 0.2 mmol triphenylphosphine in 10 mL THF.

(**38**) 0.1 mmol copper(I) oxide and 0.2 mmol hexafluoropenta-2,4-dione in 10 mL dichloromethane.

(**39**) 0.1 mmol (dimethylsulfide)copper(I) bromide and 0.1 mmol 2,2′-bipyridine and 10 mL THF.

(**40**) 0.1 mmol (dimethylsulfide)copper(I) bromide and 0.1 mmol DPPE (toluene) or 0.2 mmol triphenylphosphine (THF) and 10 mL of solvent.

The reaction mixture was frozen in liquid nitrogen and degased. 0.25 mmol of tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed to −30 °C and argon was added to the vessel for pressure compensation. The reaction mixture was stirred overnight at room temperature. After removal of all volatiles in high vacuum the residue was dissolved in dried d^8-toluene or d^8-THF. ^{19}F NMR spectra showed no evidence for the formation of a fluorine containing complex.

4.2.18. Preparation of 41

In an 8-mm-Duran-glass-tube tetrafluorobutatriene (5 mmol) was condensed onto liquid nitrogen cooled enneacarbonyl diiron (24 mg, 0.065 mmol) in 1 mL of wet dichloromethane. The tube was flame sealed and slowly warmed to room temperature. The enneacarbonyl diiron slurry turned into a clear solution within 1 h. After 3 days 2 colorless air-sensitive crystals were isolated from a grey solid. One crystal was used for X-ray crystallography and the second one for NMR- and IR-spectroscopy.

^{19}F NMR (d8-THF, $CFCl_3$): −52 (1F, $=CF_2$), −74 (1F, $=CF_2$), −74 (1F, $-CF_2-$), −110 (1F, $-CF_2-$) ppm; IR (diethylether): 2139 (s), 2090 (s), 2072 (s) cm^{-1}.

Crystal structure analysis: A suitable crystal was selected using a microscope, mounted onto glass fiber using silicon grease, and transferred into the cold gas stream of a diffractometer. BRUKER-AXS, SMART-CCD, Mo Kα, $\lambda = 0.71073$ Å, $T = 133$ K.

Crystal data for **41**: $C_{13}H_2F_6FeO_7$, $M = 440.00$, monoclinic, $a = 6.8946(19)$ Å, $b = 13.457(4)$ Å, $c = 15.899(4)$ Å, $\alpha = 90.00°$, $\beta = 90.926(7)°$, $\gamma = 90.00°$, $V = 1475.0(7)$ Å^3, $T = 173(2)$ K, space group $P2_1/n$, $Z = 4$, μ(Mo Kα) = 1.133 mm^{-1}, 11736 reflections measured, 4220 independent reflections ($R_{int} = 0.0447$). The final R_1 values were 0.0457 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1031 ($I > 2\sigma(I)$). The final R_1 values were 0.0833 (all data). The final $wR(F^2)$ values were 0.1200 (all data). The goodness of fit on F^2 was 1.020. Empirical absorption correction (SADABS), least squares refinement (SHELXL-97).

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