Iron-Catalyzed Transformations of 2-Chloro-1,6-heptadienes

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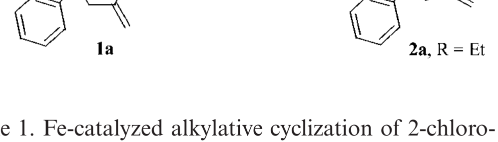
(Phosphane)iron complexes in the presence of excess trialkylaluminium reagents catalyze various transformations of 2-chloro-α,ω-dienes, depending on their structure. Most notably, in the cases of simple 2-chloro-1,6-heptadienes, cyclization with transfer of the alkyl group (Me and Et) from the corresponding trialkylaluminium compound was observed to give 2-alkyl-1-methylidenecyclopentanes. Reaction with 2-chloro-1,7-octadiene afforded the product of reductive dehalogenation. In the case of 2-chloro-4-aza-1,6-heptadiene a partial or complete hydrogenation of the double bonds was observed depending on the amount of trialkylaluminum reagent used. Interestingly, allyl(2-chloroallyl)malonate underwent C–C bond cleavage with the loss of an allyl group to give (2-chloroallyl)malonate. In the presence of ruthenium catalysts only reductive dehalogenation was observed.

Introduction

The development of efficient and cheap catalytic systems for complex transformations of organic compounds is of general synthetic interest. Iron and its compounds, because of their low cost and non-toxicity, are ideal starting materials for such a venture. In their pioneering work almost 30 years ago, Kochi and co-workers clearly showed the synthetic potential of iron-based catalysts for cross-coupling reactions.[1] However, these findings were overshadowed by the introduction of Pd catalysts. Nevertheless, in recent years there has been a revival of interest in the development of iron-based catalysis in organic synthesis. For example, iron compounds have been used as catalysts for cross coupling,[2–4] cycloadditions,[5] CO insertion,[6] carbozincation,[7] carbolithiation,[8] carboalumination,[9] conjugated addition,[10] and vinylcyclopropane rearrangement.[11] Herein we would like to present results obtained in a study of (phosphane)iron-catalyzed reactions of 2-chloro-α,ω-dienes with trialkylaluminium reagents, notably the alkylative cyclization of 2-chloro-1,6-heptadienes.[12]

Results and Discussion

Our initial interest stemmed from the fact that it would be of general synthetic interest to explore possibilities of replacing the usually expensive palladium catalysts by much cheaper iron catalysts. One such reaction that would benefit from this is the Pd-catalyzed Heck reaction, in particular its intramolecular variant: cyclization of 2-halo-1,6-dienes gives 1,3-dimethylenecycloalkanes.[13,14] For that purpose, we decided to mimic the Pd-based catalytic system by the use of a mixture of $FeCl_3/3PPh_3$ (5 mol %), with an excess of $AlEt_3$ as a reductant and carrying out the reaction in toluene at 20 °C for 36 h. Gratifyingly, a reaction was observed, although compound **2a** was formed in 57% yield instead of the expected Heck-type product (Scheme 1). The formation of compound **2**, which is the product of ethyl group transfer and cyclization, is significant, because intermolecular alkyl-group transfers during the Heck reaction under Pd catalysis are rare.[11] Moreover, no traces of the expected exocyclic 1,3-diene (the Heck reaction product) were found in the reaction mixture. This result caught our attention and we set out to check the influence of an Fe-based catalytic system on the course of the reaction. The results are summarized in Table 1.



Scheme 1. Fe-catalyzed alkylative cyclization of 2-chloro-1,6-diene (**1a**) to 2-alkyl-1-methylenecyclopentanes **2a**

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Table 1. Ligand effect on the Fe-catalyzed cyclization of **1a** to **2a**

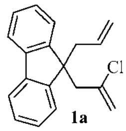
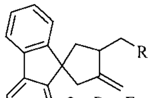
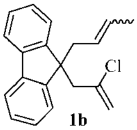
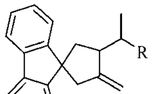
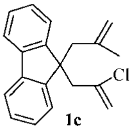
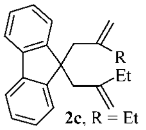
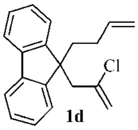
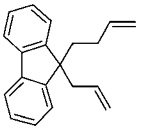
Entry[a]	Fe salt[b]	Ligand	mol %	Yield [%][c]
1	$FeCl_3$	PPh_3	15	57 (30)
2	$FeCl_3$	DPEphos	5	80 (60)
3	$FeCl_3$	dppe	5	0
4	$FeCl_3$	dppp	5	0
5	$FeCl_3$	dppb	5	34
6	$FeCl_3$	dppf	5	19
7	$FeCl_3$	$P(o\text{-tolyl})_3$	15	51
8	$FeCl_3$	$P(O)PPh_3$	15	46
9	$FeCl_3$	$P(OEt)_3$	15	47
10	$FeCl_3$	$AsPh_3$	15	56
11	$[Fe(acac)_3]$			21
12	$Fe(acac)_3]$	PPh_3	15	28
13	$[Fe(acac)_3]$	DPEphos	5	27
14	$[Fe(dbm)_3]$			40
15	$[Fe(dbm)_3]$	PPh_3	15	42
16	$[Fe(dbm)_3]$	DPEphos	5	40
17	$[FeCl_2(PPh_3)_2]$			87 (65)

[a] Reactions were carried out at 20 °C. [b] 5 mol % of iron salt was used. [c] ^1H NMR yields. Isolated yields are in parentheses.

These results clearly show that the course of the reaction is governed to a great extent by both the counterion in the Fe salt and the nature of the ligand. The good result, 80% yield of **2**, was obtained with a combination of the bidentate phosphane DPEphos and $FeCl_3$ (Entry 2). The use of other bidentate phosphanes either did not result in any reaction (Entry 3,4) or gave low yields of **2** (Entries 5, 6). Monodentate phosphanes and arsanes (Entries 7−10) gave similar results to the one obtained with PPh_3 (Entry 1). Interestingly, the use of iron(III) 1,3-dionates [$Fe(acac)_3$ and $Fe(dbm)_3$], which are known to be good catalysts for cross-coupling reactions, gave rather low yields of the cyclized product **2a** whether alone (Entries 11, 14) or in a combination with phosphanes (Entries 12, 13, 15, 16). Interestingly, the best yield of **2a** (87%) was obtained in the reaction with rather unstable [$FeCl_2(PPh_3)_2$] (Entry 17).[15] In addition, when the reaction was carried out at 80 °C, even monodentate phosphanes such as PPh_3 and P(*o*-tolyl)$_3$ were as effective as DPEphos, and compound **2a** was formed in 80 and 83% yield, respectively.

Our subsequent work was directed to check the scope of the reaction with respect to: (i) the double-bond substitution in **1**, (ii) the extent of the Me and Et group transfer, (iii) a catalytic system (ligand and metal effect), and (iv) the source of the transferable alkyl group (various alkylaluminium compounds as well as other potential organometallic reagents were tested). In this regard the cyclization was checked with variously substituted 2-chloro-1,6-heptadienes **1a−d**, with various catalytic systems under different reaction conditions. The results are summarized in Table 2. In the case of alkylative cyclization of **1a** ethyl-group transfer proceeded well with both catalytic systems **A** and **B**, furnishing **2a** in 80 and 83% yields, respectively. Methyl-group transfer proceeded well with $AlMe_3$ and catalyst **B** affording 73% of **3a**. Attempts to induce cyclization with MAO resulted only in low yields of **3a**. The structure of **3a** was unequivocally confirmed by a single-crystal X-ray analysis (Figure 1). The cyclization of chlorodiene **1b** (19:1 mixture of *trans* and *cis* isomers), bearing a 2-butenyl moiety, gave rather low yields of the corresponding products with both catalytic systems. The reaction with $AlEt_3$ gave **2b** as a mixture of diastereoisomers in a 3:1 ratio (according to ^1H and ^{13}C NMR spectroscopy) in 30% and 29% yields and with $AlMe_3$ gave **3b** in 23% and 24% yields, respectively. Interestingly, the use of MAO as the source of the methyl group did not result in any reaction. Surprisingly, attempts to carry out alkylative cyclization with **1c**, bearing a methallyl moiety, were not successful. The reaction of **1c** with $AlEt_3$ resulted in the formation of a complex reaction mixture in which only the starting material **1c** and the product of the cross-coupling reaction (**2c**; 47%) were identified by spectroscopic methods (GC-MS, NMR spectroscopy). Also, the reaction with $AlMe_3$ furnished only traces of the cross-coupling product **3c**. Similarly, the use of **1d**, bearing a 3-butenyl moiety, in the reaction with $AlEt_3$ did not give the cyclized product, instead reductive dehalogenation to **4d** was observed in 80% yield.

Table 2. Alkylative cyclization of 2-chloro-α,ω-dienes **1** in the presence of Fe catalysts and alkylaluminium reagents

Reactant	R_3Al	Catalyst	*T* [°C]	Product	Yield [%][b]
 **1a**	Et_3Al	A	20	 **2a**, R = Et **3a**, R = Me	**2a**, 80 (60)
	Et_3Al	B	80		**2a**, 83
	MAO	A	20		**3a**, 20
	MAO	B	80		**3a**, 25
	Me_3Al	A	20		**3a**, 36
	Me_3Al	B	80		**3a**, 73 (52)
 **1b**	Et_3Al	A	20	 **2b**, R = Et **3b**, R = Me	**2b**, 30 (20)[c]
	Et_3Al	B	80		**2b**, 29[c]
	MAO	A	20		**3b**, 0
	MAO	B	80		**3b**, 0
	Me_3Al	A	20		**3b**, 23 (15)
	Me_3Al	B	80		**3b**, 24
 **1c**	Et_3Al	A	20	 **2c**, R = Et **3c**, R = Me	**2c**, 47
	MAO	A	20		**3c**, 0
	Me_3Al	A	20		**3c**, < 5[d]
 **1d**	Et_3Al	A	20		**4d**, 80 (60)

[a] A = $FeCl_3$ (5 mol %)/DPEphos (10 mol %), B = $FeCl_3$ (5 mol %)/PPh_3 (15 mol %). [b] ^1H NMR yields. Isolated yields are in parentheses. [c] 3:1 mixture of diastereoisomers. [d] Yield and structure determined by GC-MS analysis.

Reaction with other stronger or weaker Lewis-acidic organometallic reagents, such as chlorodiethylaluminium ($AlClEt_2$), triethylborane (BEt_3), and diethylzinc ($ZnEt_2$), did not yield any products and the starting material remained intact. Attempts to carry out the reaction with simple α,ω-dienes were also unsuccessful.

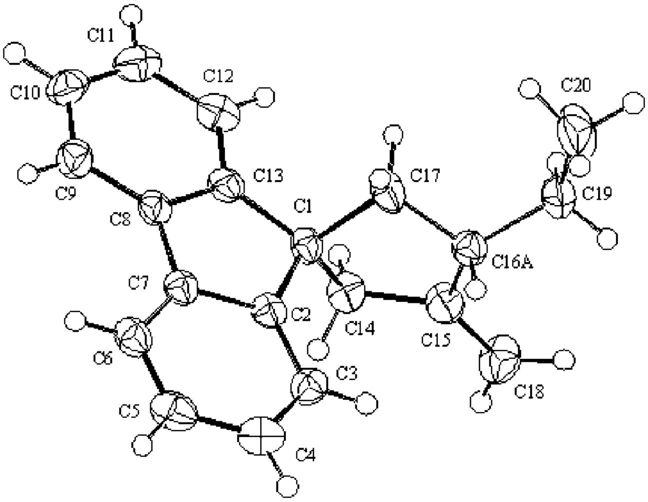
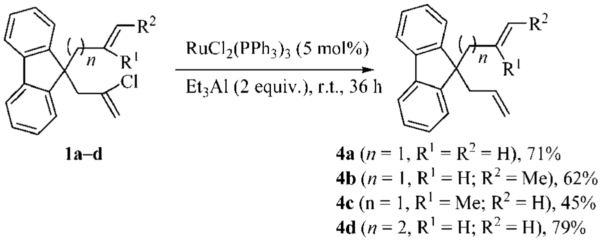


Figure 1. View of **3a** with displacement ellipsoids set at 50% probability

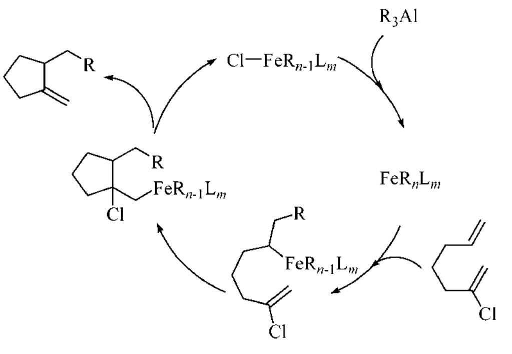
Ruthenium, which is in the same group as iron, was expected to have similar properties and, as expected, conversion of the starting materials **1a−d** was observed in the presence of a catalytic amount of [$RuCl_2(PPh_3)_3$] (5 mol %) and $AlEt_3$ (2 equiv.) at 20 °C; however, in all cases reductive dechlorination to the corresponding dienes **4a−d** took place in 45−79% yields (Scheme 2). No traces of cyclized products were detected.



Scheme 2. Ru-catalyzed reductive dehalogenation of 2-chloro-α,ω-dienes **1** to α,ω-dienes **2** and **4**

The above-mentioned results indicate that several competing reaction pathways may take place in the Fe-catalyzed cyclization and that the major one might be the result of a combination of several factors. At the first approximation it is obvious that the course of the reaction is governed by steric factors: (i) alkylative cyclization proceeds only with unsubstituted or terminally substituted dienes **1a**,**b**, and (ii) in the case of the substrate with an internally substituted double bond (**1c**) the cross-coupling reaction prevails. Secondly, a certain role may also be played by the size of the linker (i.e. formation of a five- or six-membered ring) because the reaction of diene **1d** gave only the product of reductive dehalogenation. A cooperative coordination of the double bond of the vinyl chloride moiety to the iron atom cannot be excluded.

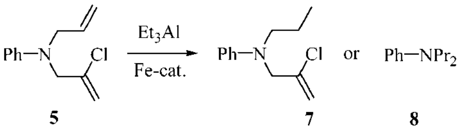
As far as the details of the reaction mechanism are concerned, there is enough evidence to suggest that the initial step of the reaction mechanism is not oxidative addition of the C−Cl bond to the reduced iron atom and that it must proceed through a different pathway. This is supported by the following facts. Firstly, attempts to achieve cross-coupling with several vinyl chlorides (cyclohexenyl chloride, β-chlorostyrene) and $AlEt_3$ were not successful. In the former case an intractable mixture was formed, and in the latter the cross-coupling product was formed in only 10% yield. Similar phenomena have been observed previously.[3b] Secondly, the reaction of **1a** with an organomagnesium reagent resulted only in the cross-coupling reaction.[4] Although we were not able to track the course of the reaction mixture by spectroscopic methods (NMR studies did not give any information), we assume that the catalytically active species is a cationic alkyliron(II) complex that is generated by the reaction of iron(III) compounds with trialkylaluminium compounds. It has been shown that iron complexes undergo alkylation[16] and reduction,[17] resulting in the formation of alkyliron(II) species. It is reasonable to expect that the excess of trialkylaluminium reagent ensures that the iron(III) complexes are converted into the cationic species.[18] However, the alkylaluminium complexes differ in their reactivity with non-stabilized alkyliron compounds.[19] The formation of cationic species is supported by the observation that the reaction does not proceed with organomagnesium or organozinc compounds. The proposed reaction mechanism is depicted in Scheme 3 and consists of the following steps: (i) formation of the cationic species, (ii) carbometalation (carboferration) of the double bond to give a secondary alkyliron compound,[20] (iii) intramolecular carbometalation of the second double bond (vinyl chloride moiety) to give a primary alkyliron compound, and, finally, (iv) β-chloride elimination to give the product and iron(II) chloride that returns back into the catalytic cycle.



Scheme 3. Proposed catalytic cycle for the iron-catalyzed alkylative cyclization

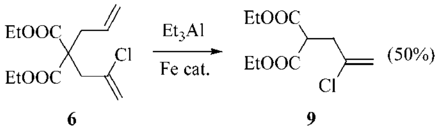
It is noteworthy to mention that the presumed carboferration step proceeds in the opposite manner to the "normal" carbometalation of alkenes[21,22] and of α,ω-dienes[22,23] observed for early transition metal catalysis (e.g. Zr). Although the true nature of this effect is not yet clear, a similar phenomenon has been observed during iron-catalyzed dimerization of 1-alkenes that resulted in the predominant formation of linear products.[20d]

Other 2-chloro-1,6-heptadienes such as **5** and **6** were tested under the same conditions as well. However, in both cases the course of the reaction took a different pathway. The reaction of **5** with triethylaluminium resulted either in partial or total reduction of the double bonds to give **7** or **8** depending on the amount of triethylaluminium used (Scheme 4). Thus, the reaction in the presence of 4 equiv. of $AlEt_3$ afforded **7** and **8** in 75 and 11% yield, respectively. When a large excess of $AlEt_3$ (8 equiv.) was used, only the formation of **8** was observed. It is worth mentioning that possible products of cross-coupling or reductive dehalogenation were not detected, and that the reduction takes place initially at the unactivated double bond.



Scheme 4. Fe-catalyzed reduction of 2-chloro-4-aza-1,6-heptadiene **7**

Interestingly, a completely different reaction pathway was observed in the case of the reaction of **6** with triethylaluminium. Instead of the expected cyclization, deallylation of **6** to **9** was observed in 47% yield (Scheme 5). The reaction proceeded very cleanly and the final reaction mixture consisted only of **9** and unchanged starting material **6**. It is necessary to emphasize that possible products of cross-coupling or reductive dehalogenation were not detected, and that this reaction proceeded only in the presence of a catalytic amount of Fe complexes. The preference for the cleavage of the unactivated C−C bond was rather unexpected and it is unique to this substrate; attempts to carry out the same reaction with other allylmalonates remained fruitless.



Scheme 5. Fe-catalyzed deallylation of allyl(2-chloroallyl)malonate **6** to (2-chloroallyl)malonate **9**

Conclusion

In summary, we have shown that 2-chloro-α,ω-dienes undergo various iron-catalyzed transformations in the presence of trialkylaluminium compounds, such as alkylative cyclization, reductive dehalogenation, cross-coupling reactions, C−C bond cleavage, or double bond hydrogenation, depending on their structural features. In this regard the most noteworthy reaction is the new and hitherto unreported alkylative cyclization accompanied by Me or Et group transfer, which proceeds through reverse carbometalation (carboferration) of the double bond. Moreover, other results indicate that there is rich synthetic potential of iron-catalyzed transformations.

Experimental Section

General Remarks: THF and toluene were distilled from sodium benzophenone ketyl. All other reagents were obtained from commercial sources. GC analyses were performed with a Shimadzu GC-17A chromatograph equipped with a ZB-5 column (5% phenyl-, 95% dimethylpolysiloxane). Infrared spectra were recorded with a Bruker IFS 88 spectrometer. ^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions with a Varian UNITY 400 INOVA spectrometer (^1H at 400 MHz, ^{13}C at 100 MHz) with $SiMe_4$ as an internal standard. Melting points (uncorrected) were determined by using a Boëtius melting point apparatus. Mass spectra were obtained with a Finnigan Mat Incos 50 instrument. All reactions were carried out under argon in oven-dried Schlenk tubes. The ^1H NMR yields were determined by using an internal standard (mesitylene). Compounds **1a−d**[24] and **5**,[25] were prepared according to previously reported procedures. Compound **6** was prepared by alkylation of allyl malonate with 2,3-dichloropropene in MeCN under basic conditions.

General Procedure for Iron-Catalyzed Reactions of 2-Chloro-α,ω-dienes with AlR_3: An AlR_3 solution in toluene or hexane (1 mmol) was added to a solution of 2-chloro-α,ω-diene (0.5 mmol), phosphane (0.075 mmol for monodentate or 0.025 mmol for bidentate phosphanes), and iron(III) salt (0.025 mmol) in dry toluene (3 mL) under argon. The reaction mixture was stirred under argon at 20 °C for 36 h. After that, it was quenched with water (1 mL) followed by 3 M HCl (3 mL). The organic layer was separated and dried (Na_2SO_4). The product was separated by column chromatography (silica gel, hexane), and purified by HPLC chromatography (silica gel; hexane).

3-Methylidene-4-propylspiro[cyclopentane-1,9′-fluorene] (2a): Chlorodiene **1a** (141 mg, 0.5 mmol), DPEPhos (13.5 mg, 0.025 mmol), $FeCl_3$ (4 mg, 0.025 mmol) and a 2 M solution $AlEt_3$ in toluene (0.5 mL, 1 mmol). Yield 80% (^1H NMR). ^1H NMR ($CDCl_3$, $SiMe_4$): δ = 0.95 (t, J = 7.2 Hz, 3 H), 1.32−1.44 (m, 2 H), 1.44−1.56 (m, 1 H), 1.81−1.91 (m, 1 H), 1.96−2.04 (m, 1 H), 2.09−2.16 (m, 1 H), 2.58 (dm, J = 16.2 Hz, 1 H), 3.04 (dm, J = 15.4 Hz, 2 H), 5.05−5.09 (m, 2 H), 7.25−7.35 (m, 4 H), 7.41−7.51 (m, 2 H), 7.68−7.72 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.29, 20.93, 38.19, 43.35, 45.41, 45.79, 55.50, 106.29, 119.62, 119.65, 122.60, 123.24, 126.90, 127.00, 127.26, 127.36, 139.23, 139.90, 151.42, 153.34, 156.14 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3070, 3039, 3023, 3018, 2961, 2930, 2874, 1449, 1223, 1217, 1206, 1200, 888 cm^{-1}. EI-MS: *m/z* (%) = 274 (80) [M^+], 231 (82), 217 (85), 203 (90), 178 (100), 165 (27). HRMS: calcd. for $C_{21}H_{22}$ 274.1721, found 274.1714. $C_{21}H_{22}$: calcd. C 91.92, H 8.08; found C 91.82, H 8.29.

4-(But-2-yl)-3-methylidenespiro[cyclopentane-1,9′-fluorene] (2b): Chlorodiene **1b** (148 mg, 0.5 mmol), DPEPhos (13.5 mg, 0.025 mmol), $FeCl_3$ (4 mg, 0.025 mmol) and a 2 M solution of $AlEt_3$ in toluene (0.5 mL, 1 mmol). Yield 30% (^1H NMR) (mixture of diastereoisomers, 3:1). Major diastereomer: ^1H NMR ($CDCl_3$, $SiMe_4$): δ = 0.94 (t, J = 7.2 Hz, 3 H), 1.00 (d, J = 6.8 Hz, 3 H), 1.19−1.30 (m, 1 H), 1.30−1.42 (m, 1 H), 1.77−1.82 (m, 1 H), 1.84−1.89 (m, 1 H), 2.20 (dd, J = 12.8, 10.8 Hz, 1 H), 2.47 (dd, J = 15.6, 1.6 Hz, 1 H), 3.00 (dm, J = 15.6 Hz, 1 H), 3.14−3.24 (m, 1 H), 5.04−5.07 (m, 1 H), 5.11−5.15 (m, 1 H), 7.21−7.46 (m, 4 H), 7.52 (d, J = 7.2 Hz, 2 H), 7.68−7.73 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.50, 17.26, 29.91, 38.81, 41.14, 46.86, 48.95, 55.38, 107.50, 119.66, 122.47, 123.31, 126.90, 127.06, 127.23, 127.33, 139.15, 140.04, 151.02, 153.34, 154.42) ppm. Minor diastereomer: ^1H NMR ($CDCl_3$, Me_4Si): δ = 0.98 (t, J = 7.2 Hz, 3

H), 1.01 (d, J = 6.8 Hz, 3 H), 1.19−1.30 (m, 1 H), 1.30−1.42 (m, 1 H), 1.59−1.72 (m, 2 H), 2.21 (dd, J = 12.8, 10.8 Hz, 1 H), 2.43 (dd, J = 15.6, 1.6 Hz, 1 H), 3.00 (dm, J = 15.6 Hz, 1 H), 3.04−3.14 (m, 1 H), 5.04−5.07 (m, 1 H), 5.11−5.15 (m, 1 H), 7.21−7.46 (m, 4 H), 7.52 (d, J = 7.2 Hz, 2 H), 7.68−7.73 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.18, 13.90, 28.19, 38.17, 39.50, 46.52, 47.27, 55.38, 106.79, 119.66, 122.47, 123.31, 126.90, 127.06, 127.23, 127.33, 139.15, 140.04, 151.02, 153.34, 155.06 ppm. IR ($CHCl_3$): ṽ = 3068, 2962, 2930, 2875, 1449, 1379, 908, 886 cm^{-1}. EI-MS: m/z (%) = 288 (12) [M^+], 233 (64), 219 (100), 203 (78), 191 (96), 178 (79), 165 (26). $C_{20}H_{20}$: calcd. C 91.61, H 8.39; found C 91.75, H 8.42.

4-Ethyl-3-methylidenespiro[cyclopentane-1,9′-fluorene] (3a): Chlorodiene **1a** (141 mg, 0.5 mmol), DPEPhos (13.5 mg, 0.025 mmol), $FeCl_3$ (4 mg, 0.025 mmol) and a 2 M solution of $AlMe_3$ in hexane (0.5 mL, 1 mmol). Yield 36% (^{1}H NMR). M.p. 53−54 °C (MeOH), ^{1}H NMR ($CDCl_3$, $SiMe_4$): δ = 0.98 (t, J = 7.5 Hz, 3 H), 1.48−1.60 (m, 1 H), 1.87−1.98 (m, 1 H), 2.01 (dd, J = 13.0, 10.4 Hz, 1 H), 2.13 (ddd, J = 13.0, 8.1, 1.7 Hz, 1 H), 2.58 (dm, J = 16.0 Hz, 1 H), 2.93−3.03 (m, 1 H), 3.04 (dm, J = 16.0 Hz, 1 H), 5.05−5.10 (m, 2 H), 7.22−7.28 (m, 1 H), 7.29−7.36 (m, 3 H), 7.41−7.46 (m, 1 H), 7.48−7.51 (m, 1 H), 7.68−7.73 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.05, 28.53, 45.15, 45.33, 45.50, 55.45, 106.46, 119.63, 119.66, 122.60, 123.27, 126.91, 127.01, 127.25, 127.36, 139.22, 139.92, 151.38, 153.35, 155.84 ppm. IR ($CHCl_3$): ṽ = 3069, 2963, 2929, 2876, 1653, 1478, 1449 cm^{-1}. EI-MS: m/z (%) = 260 (82) [M^+], 231 (88), 217 (69), 203 (99), 178 (100), 165 (31). $C_{20}H_{20}$: calcd. C 92.26, H 7.74; found C 92.26, H 7.8.

3-Methylidene-4-(2-propyl)spiro[cyclopentane-1,9′-fluorene] (3b): Chlorodiene **1b** (148 mg, 0.5 mmol), DPEPhos (13.5 mg, 0.025 mmol), $FeCl_3$ (4 mg, 0.025 mmol) and a 2 M solution of $AlMe_3$ in hexane (0.5 mL, 1 mmol). Yield 23% (^{1}H NMR). ^{1}H NMR ($CDCl_3$, $SiMe_4$): δ = 1.00 (d, J = 6.4 Hz, 3 H), 1.01 (d, J = 6.4 Hz, 3 H), 1.89 (ddd, J = 12.8, 8.0, 2.0 Hz, 1 H), 2.09−2.17 (m, 1 H), 2.21 (dd, J = 13.6, 10.8 Hz, 1 H), 2.46 (d, J = 15.2 Hz, 1 H), 2.97−3.01 (m, 1 H), 3.01−3.08 (m, 1 H), 5.06−5.09 (m, 1 H), 5.12−5.15 (m, 1 H), 7.21−7.47 (m, 4 H), 7.50−7.54 (m, 2 H), 7.70−7.74 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.4, 21.1, 31.6, 40.2, 46.5, 49.4, 55.3, 107.4, 119.6, 119.7, 122.5, 123.3, 126.9, 127.1, 127.2, 127.3, 139.1, 140.0, 151.0, 153.3, 154.6 ppm. IR ($CHCl_3$): ṽ = 3067, 2958, 2931, 2872, 1688, 1656, 1641, 1449, 884 cm^{-1}. EI-MS: m/z (%) = 274 (82) [M^+], 231 (100), 217 (47), 203 (64), 178 (97), 165 (33). HRMS calcd. for $C_{21}H_{22}$: 274.172151; found 274.172567.

X-ray Crystallographic Study: A suitable colorless crystal of dimension 0.45 × 0.35 × 0.15 mm obtained upon slow evaporation of the solvent from a solution of **3a** in methanol was used for data collection with a Nonius Kappa CCD diffractometer equipped with an Oxford cryostream cooler at 150 K. Crystal data: a = 17.3650(5), b = 6.8520(2), c = 12.9910(3) Å, β = 99.8540(17)°; Z = 4, monoclinic $C2$, Mo-K_α radiation, λ = 0.71070 Å, $D_{calcd.}$ = 1.136 Mg·m^{-3}. 3429 independent reflections. The structure was solved by direct methods (SIR97)[31] and refined by weighted full-matrix least squares on F^2 (SHELXL-97).[32] Final R and ωR were 0.0412 and 0.1040, respectively. CCDC-211049 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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