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Palladium(II) allylic complexes by carbene transmetalation and migratory insertion reactions: Synthesis and side reactions

Ana C. Albéniz *, Pablo Espinet *, Alberto Pérez-Mateo

IU CINQUIMA/Química Inorgánica, Universidad de Valladolid, 47071 Valladolid, Spain

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ABSTRACT

New 1,1-alkoxy, aryl substituted palladium η^3-allyls $[Pd(\mu\text{-}Br)\{\eta^3\text{-}C(C_6F_5)(OMe)CHR^1CHR^2\}]_2$ can be synthesized from $[W(CO)_5\{C(OMe)CHR^1{=}CHR^2\}]$ and a palladium perfluoroaryl complex. The allyls are formed by transmetalation of the carbene fragment followed by migratory insertion of C_6F_5 to the putative and highly reactive Pd carbene complex. This reaction pathway predominates in all cases, but insertion of the double bond of the tungsten alkoxyvinylcarbenes into the Pd–C_6F_5 bond leads to secondary products, namely $C_6F_5(OMe)C{=}CR^1CH(C_6F_5)R^2$.

1. Introduction

The migratory insertion reaction of an aryl group to a carbene in the palladium coordination sphere is a process that readily occurs for electrophilic carbene fragments, such as those bearing only one heteroatom-containing substituent. Since few palladium carbenes of this type are known, the migratory insertion reaction has been rarely observed [1–3]. We have reported that transmetalation of carbene fragments $\{CXR^1\}$ (X = NR_2, OR; R^1 = hydrocarbyl) from tungsten to palladium can be used as a synthetic route for palladium carbenes [1,4,5]. When the palladium complex contains a Pd–aryl moiety, migratory insertion follows leading to a carbene–aryl coupling product [1,4]. This is specially fast for methoxy carbene fragments and the $[PdR^2\{C(OMe)R^1\}X]_2$ intermediate cannot be detected. Using R^1 = CH=CHPh and R^2 = C_6F_5, we could isolate the alkyl palladium migratory insertion product as a stable palladium η^3-allyl, $[Pd(\mu\text{-}Br)\{\eta^3\text{-}C(C_6F_5)(OMe)CHCHPh\}]_2$ [1b].

Following these results, we describe here the reactions of a palladium pentafluorophenyl complex with several tungsten vinylic carbenes and the formation, by transmetalation and migratory insertion, of the corresponding palladium allyls. Although palladium allyls can be synthesized by a variety of available and convenient ways [6], this is a novel route that leads to η^3-allyls with an unusual 1,1-substitution pattern. Besides this example, Kurosawa et al. described the reaction of a Pd(I) complex with a bridging vinylic carbene and $SnPh_4$ that leads to $[Pd(\eta^3\text{-}CPh_2CHCH_2)Cl(PPh_3)]$ and presumably follows a migratory insertion mechanism of the Ph group to a palladium carbene [7].

A second reaction center, the C–C double bond, is present in the vinylic tungsten carbenes and should also be considered in these reactions, since the formation of minor products through insertion of the C=C bond into the Pd–C_6F_5 bond is also observed.

2. Results and discussion

The reaction of the tungsten vinylic carbenes **1a–d**, with the palladium complex **2** leads to a series of palladium allyls **3a–d** (Scheme 1). Complex **3a** has been described by us before [1b]. Along with complexes **3**, the vinylic ethers **4** were identified. The reactions were monitored by NMR and Scheme 1 collects the molar percentages of the products in the reaction mixtures, as determined by integration of ^{19}F signals in the ^{19}F NMR spectra. Aside from **1a**, the reactions with the other tungsten carbenes are not very clean and some decomposition products coming from **2**, such as C_6F_5H and $[Pd(C_6F_5)_2(NCMe)_2]$ were also formed, along with other unidentified products. This lowers the yields of the allylic palladium complexes **3b–c**.

Complexes **3** are formed by transmetalation of the carbene fragment and migratory insertion in a putative palladium carbene (Scheme 2). The formation of this carbene has been supported by isolation of the analogous diethylaminocarbenes, which undergo a similar subsequent reactivity [4].

* Corresponding authors. Tel.: +34 983 184621; fax: +34 983 423013.
E-mail addresses: albeniz@qi.uva.es (A.C. Albéniz), espinet@qi.uva.es (P. Espinet).

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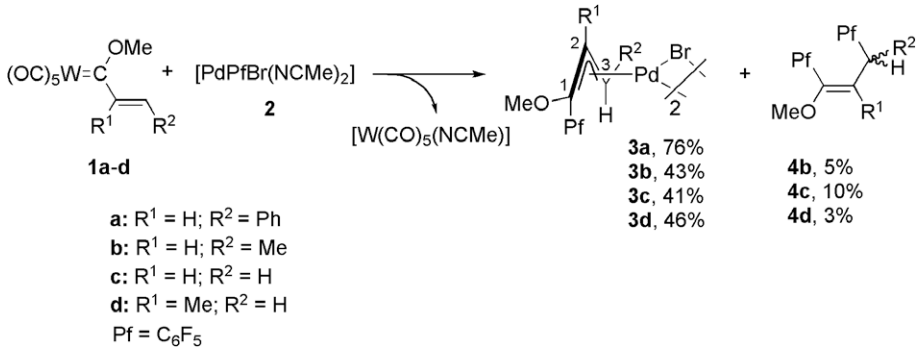
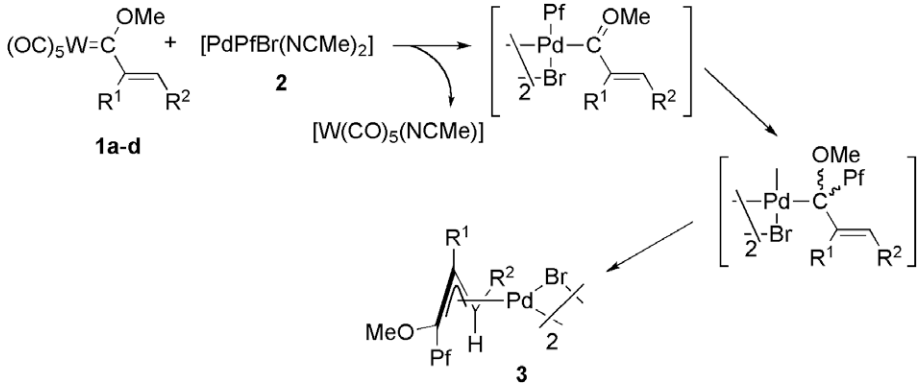
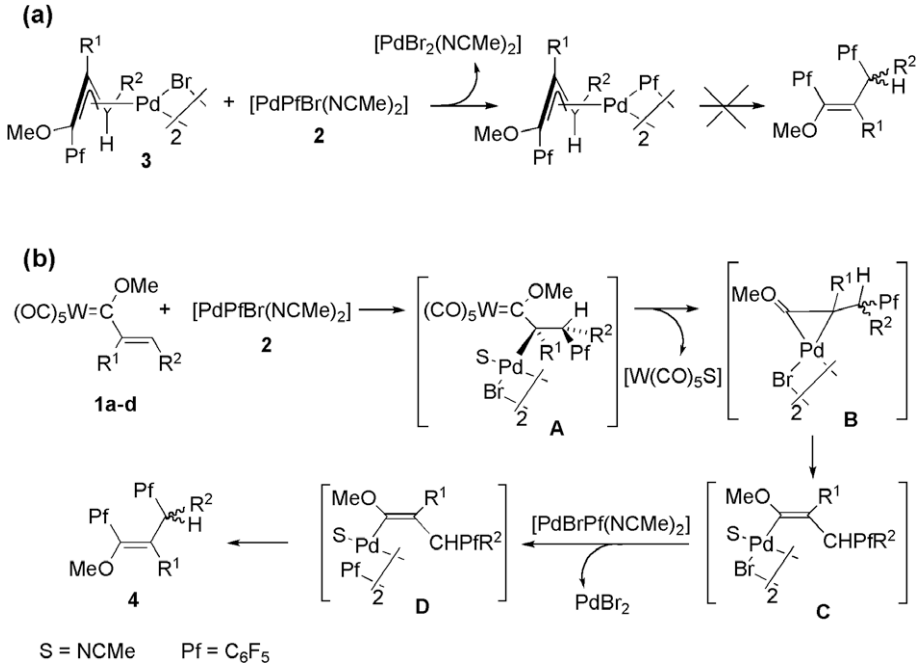


Scheme 1. Reaction of complexes **1** and **2**.



Scheme 2. Reaction pathway for the formation of **3**.

The second product, **4**, contains two C_6F_5 groups and must come from a different route. The possibility of an allyl–C_6F_5 coupling in the course of the reaction, by pentafluorophenyl transmetalation and subsequent reductive elimination, was discarded since decomposition of **3b** or **3c** in the presence of **2** does not give **4** (Scheme 3, a). The reductive elimination of an allyl and an aryl fragment is a



Scheme 3. Possible routes for the formation of **4**.

slow coupling favored in the presence of electron withdrawing ligands [8,9]. We have observed that the transmetalation of a carbene fragment from [W(CO)$_5$(carbene)] to palladium occurs with the concomitant transfer of CO, a potential electron withdrawing ligand. However, CO does not promote the allyl–C_6F_5 coupling and, again, the reaction of **3b** and **2** in the presence of CO does not give **4**. A different route must then operate, and we propose an insertion of the double bond into the Pd–C_6F_5 bond, followed by intramolecular transmetalation of the carbene (Scheme 3, b). This would give a metalacyclopropene (**B**) that could rearrange to an alkenyl complex (**C**). The second C_6F_5 group would be introduced by transmetalation from other palladium complex and reductive elimination (Scheme 3, b). Insertion of C=C bonds into Pd–C_6F_5 bonds is well documented [10], as well as fluoroaryl group exchange between palladium centers [11]. Palladium metalacyclopropenes of type **B** (Scheme 3, b) have not been reported but this type of metalacycles has been isolated for group 8 metals.

Compound **4** is a minor product of the reaction in all cases. Its final ratio depends on the substitution of the carbene double bond, the least substituted one (c, $R^1 = R^2 = H$) leading to a higher percentage of **4** (Scheme 1). This is consistent with the insertion of the C=C bond into the Pd–C_6F_5 bond being the first step in the formation of **4**.

The relative importance of the transmetalation of the carbene vs. the insertion of the C=C bond is difficult to quantify, as the crude reaction mixture contains some compounds with a pentafluorophenyl group bound to C that we could not identify [12], and could derive from either route. Nonetheless, complexes **3** are the major products of the reactions in all cases and substitution of the double bond with a phenyl group (complexes a) makes insertion of the double bond unimportant (76% of **3a** obtained). This points to transmetalation of the carbene as the main reaction pathway for the reaction of vinylic carbenes.

Complexes **3** where characterized by NMR spectroscopy and show the same stereochemistry as **3a**, whose molecular structure was previously determined by X-ray diffraction [1b]. The η^3-allyls have an *anti*-C_6F_5 *syn*-OMe and a *syn*-R^2 stereochemistry. The *anti*-C_6F_5 arrangement is characterized by a ^{19}F NMR downfield shift for the F_{ortho} signals (−127 and −136 ppm vs. −142 ppm for a typical C–C_6F_5 group) and this congested position leads to hindered rotation about the C–C_6F_5 bond in all the complexes. The arrangement of the allylic substituents was confirmed by an NOE experiment on complex **3b** that shows the proximity of the central H with the *syn*-Me (6% NOE) and the *syn*-OMe groups (11% NOE). As has been observed for other η^3-allylic complexes, compounds **3** are a mixture of isomers in solution due to the *cis–trans* arrangement of both allyl groups in the dimer [1b,10b]. Four diastereoisomers are expected from the *cis–trans* arrangement of both central C2 and both external C1 (or C3) in the allylic groups. The isomers interconvert at a rate dependent on the concentration and temperature [13]. Fig. 1 depicts the F_{ortho} region in the ^{19}F NMR spectra of **3b**, showing signals due to the four possible isomers at 223 K and fast exchange of all of them at 293 K. The monomeric acac derivative [Pd(η^3-CPf(OMe)CHCHPh)(acac)] (**5a**) does not show this isomerism and just one species is observed in solution.

Besides the process just described, **3c** shows a fast *syn–anti* interconversion of the two H^3 hydrogens at room temperature. At 213 K the exchange is slow enough to detect both *syn*-H^3 and *anti*-H^3 as separated and well resolved signals. *Syn–anti* exchange is a common fluxional process for palladium allyls but it is noticeably faster for **3c** than for other halogen bridged Pd allyls. This reflects the very different substitution pattern on both ends of the allyl moiety of **3c** that seems to favor the σ-C^3 coordination of the allyl that triggers the exchange [6,14].

3. Conclusion

New 1,1-alkoxy, aryl substituted palladium η^3-allyls can be synthesized from tungsten alkoxyvinylcarbenes and a palladium perfluoroaryl complex. The allyls are formed by transmetalation of the carbene fragment followed by migratory insertion of C_6F_5 to the new and highly reactive Pd carbene complex. This reaction pathway predominates in all cases, but insertion of the double bond of the tungsten alkoxyvinylcarbenes into the Pd–C_6F_5 bond leads to secondary products. Although the insertion route is less important than the transmetalation one, its incidence increases for double bonds with no or small substituents.

4. Experimental

4.1. General methods

All manipulations were carried out using Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts are referenced to TMS for ^{1}H and ^{13}C and to $CFCl_3$ for ^{19}F. The spectral data were recorded

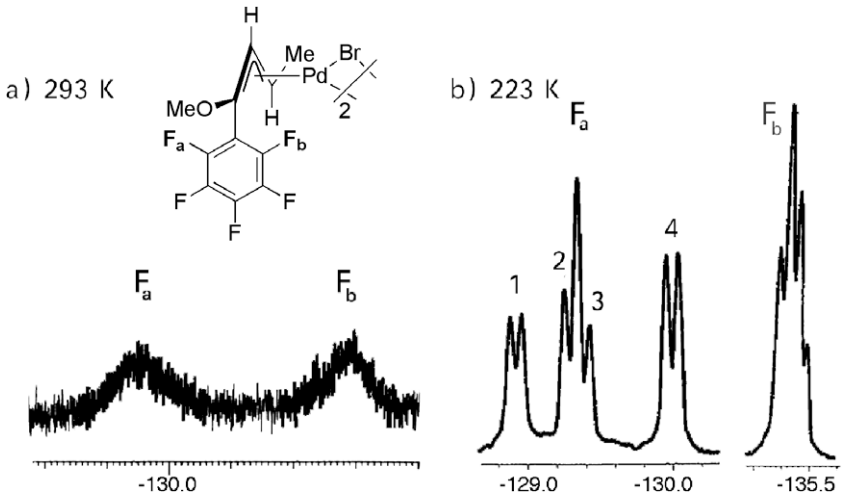


Fig. 1. F_{ortho} signals in the ^{19}F NMR spectra of **3b** at different temperatures, showing the expected four isomers of a non-symmetrical allylic dimeric complex (b). Restricted rotation leads to inequivalent F_{ortho} atoms (a and b).

at 293 K unless otherwise stated. C, H and N elemental analyses were performed on a Perkin–Elmer 240 microanalyzer. Compounds **1a** [15], **1b–d** [16], **2** [10b], were prepared according to literature methods. Complex **3a** has been described before [1b]. Percentages of products in the reactions mixtures were determined by integration of ^{19}F NMR signals.

4.2. Synthesis of complexes **3**

4.2.1. [Pd(μ-Br){(η³-C(C₆F₅)(OMe)CHCHMe}]₂ (**3b**)

To a solution of **1b** (0.250 g, 0.613 mmol) in CH_2Cl_2 (10 mL) was added **2** (0.2668, 0.613 mmol) and the mixture was stirred for 4 h at room temperature. The resulting dark suspension was filtered through activated carbon and the filtrate was evaporated to dryness. The residue was triturated with *n*-pentane and the yellow solid was filtered, washed with *n*-pentane and vacuum-dried. (0.116 g; yield: 42%). Two isomers of the dimeric complexes (**3b** and **3b′**) can be distinguished in some NMR spectra at room temperature (see text). ^1H NMR (300 MHz, δ, $CDCl_3$): 5.30 (d, $^3J_{H-H}$ = 11.4 Hz, 1H; H^2), 3.81 (s, 3H; OCH_3), 3.47 (m, 1H; H^3), 1.45 ppm (d, $^3J_{H-H}$ = 6.2 Hz, 3H; Me); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163 (b, 2F; F_{meta}), −152.0 (t, 1F; F_{para}, **3b**), −151.9 (t, 1F, F_{para}, **3b′**), −136.0 (b, 1F, F_{ortho}), −131.0 (b, 1F, F_{ortho}); $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$, 263 K): 143.0–137.0 (*o*, *m*, *p*-Pf), 113.3 (s; C^1OMe), 110.5 (*i*-Pf), 90.2 (s, C^2H, **3b**), 90.1 (s, C^2H, **3b′**), 71.0 (b, C^3HMe), 57.2 (s, OCH_3), 18.3 ppm (s, CH_3); Anal. Calc. for $C_{22}H_{16}Br_2F_{10}O_2Pd_2$: C, 30.20; H, 1.84. Found: C, 30.27; H, 2.14%.

Complexes **3c** and **3d** were prepared in a similar way. Complex **3c** (28% yield) is mixed with a small amount of other unidentified products that could not be separated by conventional methods. Complex **3d** (30% yield) was further purified by chromatography in a silica column using Et_2O as eluent.

4.2.2. Data for **3c**

Two isomers (**3c** and **3c′**) can be distinguished in some NMR spectra (see text). ^1H NMR (300 MHz, δ, $CDCl_3$): 5.35 (t, $^3J_{H-H}$ = 9.5 Hz, 1H; H^2), 3.80 ppm (s, 3H, OCH_3); ^1H NMR (300 MHz, δ, $CDCl_3/CD_3CN$, 213 K): 5.19 (dd, $^3J_{H-H}$ = 11, 8 Hz, 1H; H^2), 3.40 (s, 3H, OCH_3), 3.35 (m, $^3J_{H-H}$ = 8 Hz, 1H; *syn*-H^3), 2.20 ppm (da, $^3J_{H-H}$ = 11 Hz, 1H; *anti*-H^3); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −161.0 (ma, 2F, F_{meta}, **3c**/**3c′**), −151.1 (m, 1F, F_{para}, **3c**), −150.8 (m, 1F, F_{para}, **3c′**), −136 (ma, 1F, F_{ortho}, **3c**/**3c′**), −130.0 ppm (ma, 1F, F_{ortho}, **3c**/**3c′**).

4.2.3. Data for **3d**

Two isomers (**3d** and **3d′**, in a 1:2 ratio) can be distinguished in some NMR spectra (see text). ^1H NMR (300 MHz, δ, $CDCl_3$): 3.82 (b, 1H; *syn*-H^3), 3.55 (s, 3H; OCH_3), 2.41 (b, 1H; *anti*-H^3), 2.33 ppm (s, 3H; Me); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −161.1 (b, 2F, F_{meta}, **3d**), −160.6 (b, 1F, *m*-Pf, **3d′**), −150.6 (t, 1F, F_{para}, **3d**), −150.2 (t, 1F, F_{para}, **3d′**), −136.5 (b, 1F, F_{ortho}, **3d**/**3d′**), −128.5 (m, 1F, F_{ortho}, 3d), −127.7 ppm (m, 1F, F_{ortho}, **3d′**). Anal. Calc. for $C_{22}H_{16}Br_2F_{10}O_2Pd_2$: C, 30.20; H, 1.84. Found: C, 30.55; H, 2.15%.

4.3. Synthesis of [Pd{(η³-C(C₆F₅)(OMe)CHCHPh}(acac)] (**5a**)

To a solution of **3a** (0.250 g, 0.250 mmol) in CH_2Cl_2 (25 mL) at −30 °C was added Tl(acac) (0.2124 g, 0.697 mmol). The mixture was stirred for 1 h protected from light and then filtered through activated carbon keeping the temperature below −20 °C. The filtrate was evaporated to dryness and the residue was extracted with *n*-pentane. The pentane solution was evaporated to c.a. 5 mL and cooled to −20 °C. A yellow solid crystallizes (36.6 mg; yield: 14%). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.54 (m, 2H; Ph), 7.35 (m, 3H; Ph), 5.89 (d, $^3J_{H-H}$ = 11 Hz, 1H; H^2), 5.26 (s, 1H; H acac), 4.10 (d, $^3J_{H-H}$ = 11 Hz, 1H; H^3), 3.84 (s, 3H; OCH_3), 2.00 (s, 3H; CH_3 acac), 1.76 ppm (s, 3H; C′H_3 acac); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.4 (ma, 2F; F_{meta}), −152.8 (t, 1F; F_{para}), −137.0 (ma, 1F; F_{ortho}), −132.7 (ma, 1F; F_{ortho}); $^{13}C\{^1H\}$ NMR (75.4 MHz, δ, $CDCl_3$, 273 K): 188.2 (s, C–Me acac), 187.4 (s, C′-Me acac), 150.0–125.0 (*o*-, *m*-, *p*-Pf), 137.5 (s, *i*-Ph), 128.9 (s, *m*-Ph), 127.7 (s, *p*-Ph), 127.6 (s, *o*-Ph), 111.3 (t, $^2J_{C-F}$ = 18.9 Hz, *i*-Pf), 103.9 (s, C^1OMe(Pf)), 99.7 (s, CH acac), 87.8 (s, C^2H), 65.1 (s, C^3HPh), 56.3 (s, OCH_3), 28.1 (s, CH_3 acac), 28.0 ppm (s, C′H_3 acac); Anal. Calc. for $C_{21}H_{17}F_5O_3Pd$: C, 48.62; H, 3.30. Found: C, 48.94; H, 3.51%.

4.4. Characterization of compounds **4**

The equimolar reactions of **1b–d** and 2 (0.1 mmol) in CH_2Cl_2 were monitored by ^{19}F NMR. When complex **2** was consumed, the mixture was filtered through activated carbon and the filtrate evaporated to dryness. The residue was triturated with pentane to obtain complexes **3** (see above) and the mother liquors were evaporated. The residue was purified by column chromatography through silica using a mixture of pentane/CH_2Cl_2 (1:1) as eluent. Compounds **4** were spectroscopically characterized and **4b** was separated as a pale yellow oil.

4.4.1. (C₆F₅)(OMe)C=CH{CH(Me)(C₆F₅)} (**4b**)

^1H NMR (300 MHz, δ, $CDCl_3$): 5.30 (dt, $^3J_{H-H}$ = 9.0 Hz, $^5J_{H-F}$ = 2.1 Hz, 1H, H^2), 4.55 (q, $^3J_{H-H}$ = 9.0 Hz, 1H, H^3), 3.39 (s, 3H, OCH_3), 1.45 (d, $^3J_{H-H}$ = 9.0 Hz, 3H, Me); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −162.9 (m, 2F, F^3_{meta}), −161.8 (m, 2F, F^1_{meta}), −158.1 (t, 1F, F^3_{para}), −153.0 (t, 1F, F^1_{para}), −143.7 (m, 2F, F^1_{ortho}), −140.1 (m, 2F, F^3_{ortho}); EI (70 eV): *m*/*z* (relative intensity), 418 (M^+, 42), 403 (91), 211 (21), 195 (100), 181 (98), 167 (44).

4.4.2. (C₆F₅)(OMe)C=CH{CH₂(C₆F₅)} (**4c**)

^1H NMR (300 MHz, δ, $CDCl_3$): 5.00 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, H^2), 3.70 (d, 2H, CH_2), 3.49 (s, 3H, OCH_3); ^{19}F NMR (282 MHz, δ, $CDCl_3$): −163.0 (m, 2F, F^3_{meta}), −161.8 (m, 2F, F^1_{meta}), −157.7 (t, 1F, F^3_{para}), −152.9 (t, 1F, F^1_{para}), −144.0 (m, 2F, F^1_{ortho}), −140.0 ppm (m, 2F, F^3_{ortho}).

4.4.3. (C₆F₅)(OMe)C=CMe{CH₂(C₆F₅)} (**4d**)

^{19}F NMR (282 MHz, δ, $CDCl_3$): −157.4 (t, 1F, F^3_{para}), −152.7 (t, 1F, F^1_{para}), −141.8 (m, 2F, F^1_{ortho}), −139.1 (m, 2F, F^3_{ortho}).

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