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Reactions of $IrXL_2(PR_3)$ (X = Cl, OTf; L_2 = TFB, 2CO) with $HSnR_3$ (R = Ph, ^nBu)

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Abstract

The reactions of several square-planar $IrXL_2(PR_3)$ complexes with $HSnR_3$ have been studied. The oxidative addition of $HSnPh_3$ to the complexes $IrCl(TFB)(PR_3)$ (TFB = tetrafluorobenzobarrelene, $PR_3 = PCy_3$ (**2**), P^iPr_3 (**3**), $^iPr_2PCH_2CH_2OMe$ (**4**)) leads to the hydrido-stannyl derivatives $IrClH(SnPh_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**5**), P^iPr_3 (**6**), $^iPr_2PCH_2CH_2OMe$ (**7**)), while the reactions of **2** and **3** with HSn^nBu_3 afford $IrH_2(Sn^nBu_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**8**), P^iPr_3 (**9**)). The tetrafluorobenzobarrelene diolefin of **2-4** can be displaced by carbon monoxide to afford $IrCl(CO)_2(PR_3)$ ($PR_3 = PCy_3$ (**10**), P^iPr_3 (**11**), $^iPr_2PCH_2CH_2OMe$ (**12**)). Similarly to **2-4**, complexes **10-12** add $HSnPh_3$ to give $IrClH(SnPh_3)(CO)_2(PR_3)$ ($PR_3 = PCy_3$ (**13**), P^iPr_3 (**14**), $^iPr_2PCH_2CH_2OMe$ (**15**)), which can also be prepared from **5-7** by reaction with carbon monoxide. On treatment with AgOTf, **2** and **3** give $Ir(OTf)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**16**), P^iPr_3 (**17**)), which in the presence of $HSnPh_3$ lead to $IrH(OTf)(SnPh_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**18**), P^iPr_3 (**19**)).

Keywords: Iridium; Hydride; Stannyl; Oxidative addition

1. Introduction

The stereoselective formation of vinylstannanes by addition of alkyl- or arylstannanes to alkynes requires the presence of transition metal catalysts [1–5]. In the search for transition-metal complexes which are catalytically active in the hydrostannation of terminal alkynes, we have previously reported the reactivity of several square-planar iridium(I) compounds towards stannanes. Recently, we characterized the five-coordinate complex $Ir(SnPh_3)(CO)_3(PCy_3)$, which is generated from the reaction of $Ir\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PCy_3)$ with $HSnPh_3$. The complex $Ir(SnPh_3)(CO)_3(PCy_3)$ reacts with molecular hydrogen to give $IrH_2(SnPh_3)(CO)_2(PCy_3)$ and with $HSnPh_3$ to afford $IrH(SnPh_3)_2(CO)_2(PCy_3)$, which is isolated as the mixture of both *cis*- and *trans*-bisstannyl isomers [6]. Subsequently, we observed that the reactions of the alcohoxide complexes $Ir(OR)(TFB)(PCy_3)$ (R = Me, Et, ^{i}Pr, Ph) and the thiopropoxide compound $Ir(S^nPr)(TFB)(PCy_3)$ with $HSnPh_3$ and HSn^nBu_3 lead to the dihydrido derivatives $IrH_2(SnR'_3)(TFB)(PCy_3)$ (R′ = Ph, ^{n}Bu) and $R'_3Sn(XR)$ (X = O, S), while the alkynyl complexes $Ir(C_2Ph)L_2(PCy_3)$ (L_2 = TFB, 2CO) add the same stannanes to afford the corresponding hydrido-alkynyl $Ir(C_2Ph)H(SnR'_3)L_2(PCy_3)$, which have been found to promote the tin-carbon bond formation in the hydrostannation of phenylacetylene [7]. Most recently, we have also observed that the oxidative addition of $HSnPh_3$ to the acetylacetonato-complex Ir(acac)(cyclooctene)(PCy_3) gives rise to the five-coordinate-iridium(III) compound $Ir(acac)H(SnPh_3)(PCy_3)$ or to the six-coordinate $Ir(acac)H(SnPh_3)(PCy_3)_2$ derivative, when the reaction is carried out in the presence of tricyclohexylphosphine [8].

As a continuation of our work in this field, we now report the reactivity of the square-planar iridium(I) complexes $IrClL_2(PR_3)$ (L_2 = TFB, 2CO; $PR_3 = PCy_3$, P^iPr_3, $^iPr_2PCH_2CH_2OMe$) and $Ir(OTf)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) towards $HSnPh_3$ and HSn^nBu_3.

2. Results and discussion

2.1. Reactions of $IrCl(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3, $^iPr_2PCH_2CH_2OMe$) with $HSnPh_3$ and HSn^nBu_3

We have previously reported that on treatment with PCy_3 and P^iPr_3, the bis(tetrafluorobenzobarrelene)iridium(I) compound $IrCl(TFB)_2$ (**1**) affords the square-

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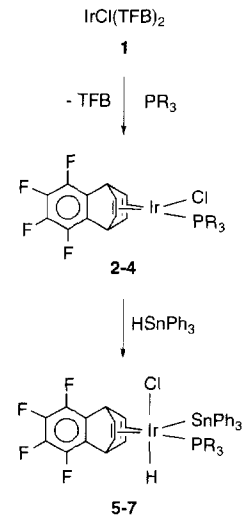
planar derivatives $IrCl(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**2**), P^iPr_3 (**3**)) [9]. Similarly, the reaction of **1** with the etherphosphine $^iPr_2PCH_2CH_2OMe$ leads to $IrCl(^iPr_2PCH_2CH_2OMe)(TFB)$ (**4**), which was isolated as an orange solid in 86% yield. The η^1-phosphorus coordination bonding mode of the phosphine ligand in this complex is strongly supported by the ^1H NMR spectrum in benzene-d_6, which shows the resonance corresponding to the protons of the methoxy group as a singlet at 2.83 ppm, a similar chemical shift to that previously reported for the free phosphine (δ 2.96) [10]. In addition, at 3.87 and 1.62 ppm, the spectrum contains two vinylic resonances for the olefinic protons of the diene, in agreement with the square-planar structure proposed in Scheme 1.

Treatment of orange toluene or chloroform solutions of **2-4** with ca. 1 equiv. of $HSnPh_3$ leads immediately to the formation of light yellow solutions, from which the hydrido-complexes **5-7** (Scheme 1) were separated as white solids in high yield (60-90%). The stereochemistry proposed for these compounds in Scheme 1 was inferred from the IR, ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra. The IR spectra show the ν(Ir-H) band at about 2200 cm^{-1}. The trans configuration of the hydrido and chloride ligands is mainly supported by the significant change in the frequencies of the ν(Ir-H) vibrations, which appear at higher frequency (ca. 80 cm^{-1}) compared with that found for the related complex $Ir(C_2Ph)H(SnPh_3)(TFB)(PCy_3)$ (2113 cm^{-1}), where the hydrido ligand is disposed trans to the diene [7]. Furthermore, the ν(Ir-H) frequencies of **5-7** agree well with



PR_3	complex
PCy_3	2, 5
P^iPr_3	3, 6
$^iPr_2P(CH_2)_2OMe$	4, 7

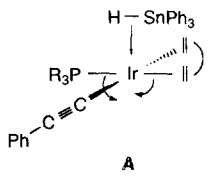
Scheme 1.

those previously reported for iridium(III) complexes with a trans H-Ir-Cl disposition [11]. In the ^1H NMR spectra the hydrido ligands give rise to doublets at about -16.5 ppm, with satellites due to the active tin isotopes. With regard to the values of the P-H (between 16.2 and 18 Hz) and Sn-H (between 21 and 55 Hz) coupling constants, there is no doubt that the hydrido ligands are disposed cis to both the phosphine and stannyl groups. The $^{31}P\{^1H\}$ NMR spectra show singlets at -3.9 (**5**), 6.7 (**6**) and 9.1 (**7**), which under off-resonance conditions split into doublets as a result of the P-H coupling with only one hydrido ligand. Near the singlets the satellites due to the active isotopes are also observed. The value of the Sn-H coupling constants, 84 Hz for the three compounds, indicates that the phosphine ligands lie cis to the triphenylstannyl group.

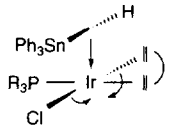
The presence of four different monodentate ligands in **5-7** produces molecules with no symmetry. In agreement with this, the ^1H NMR spectra show six resonances for the diene protons, two aliphatic resonances between 5.79 and 4.74 and four vinylic resonances between 4.76 and 3.43 ppm. In keeping with the ^1H NMR spectra the $^{13}C\{^1H\}$ NMR spectra of **5** and **6** contain four resonances for the olefinic carbon atoms of the dienes. In the spectrum of **5** the carbon atoms of the carbon-carbon double bond disposed trans to the tricyclohexylphosphine ligand appear at 77.4 ppm and 63.9 ppm as doublets with P-C coupling constants of 13.9 Hz and 8.1 Hz respectively, whereas those trans to the stannyl group are observed as singlets at 68.7 ppm and 65.6 ppm. In the $^{13}C\{^1H\}$ NMR spectrum of **6** the olefinic carbon atoms disposed trans to the triisopropylphosphine ligand appear at 77.2 ppm and 63.7 ppm, as doublets with P-C coupling constants of 14.2 Hz and 7.3 Hz respectively, and the olefinic carbon atoms trans to the stannyl group lie at 69.7 ppm and 65.6 ppm, as singlets. With the resonances corresponding to the carbon atoms of the carbon-carbon double bonds disposed trans to the stannyl group, the satellites due to the active tin isotope are clearly observed. The values of the C-Sn coupling constants (86 and 52 Hz (**5**), and 85 and 50 Hz (**6**)) confirm the mutually trans disposition of the stannyl group and one olefinic bond of the diene.

The oxidative addition of molecular hydrogen and Group 14 element hydrido compounds to iridium(I) complexes is generally viewed as a concerted cis addition [12]. Furthermore, it has been proved that the addition of $HSiR_3$ to iridium(I) bisphosphine complexes, IrX(CO)(dppe) (X = Br, CN), is a diastereoselective process with specific substrate orientation [13]. In this line, recently, we have observed that the oxidative addition of $HSnR_3$ to the alkynyl complexes $Ir(C_2Ph)L_2(PCy_3)$ (L_2 = TFB, 2CO) is also a diastereoselective process with specific substrate orientation. Thus, the oxidative addition of $HSnPh_3$ to $Ir(C_2Ph)(TFB)(PCy_3)$ takes place along the olefin-Ir-P

axis with the tin atom on the olefinic bond (**A**). The formed hydrido-alkynyl complex $IrH(C_2Ph)(SnPh_3)(TFB)(PCy_3)$ contains the hydrido ligand trans to the diene and the phosphino and stannyl groups are also trans disposed [7]. The formation of **5-7** by addition of $HSnPh_3$ to **2-4** also seems to be a concerted cis addition with specific substrate orientation. However, the stereochemistry of **5-7**, with the hydrido and the stannyl group trans disposed to the chlorine and diene respectively, suggests that the addition to **2-4** does not occur in a similar manner, approach of the substrate along to the olefin-Ir-P axis, but via an olefin-Ir-Cl orientation with the tin atom on the chlorine (**B**).



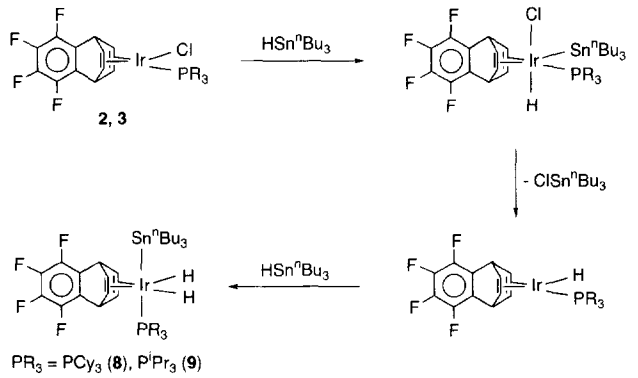
A



B

Complexes **2** and **3** also react with HSn^nBu_3. However, in contrast to the addition of $HSnPh_3$, the reactions lead to the dihydrido stannyl derivatives $IrH_2(Sn^nBu_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**8**), P^iPr_3 (**9**)). When the reactions are carried out in a 1:1 molar ratio, mixtures of the starting materials and the dihydrido products are obtained, while the quantitative formation of **8** and **9** was determined by NMR spectroscopy when 2 equiv. of HSn^nBu_3 were added to NMR tubes containing toluene-d_8 solutions of **2** and **3**. The formation of **8** and **9** most probably involves the oxidative addition of the stannane to the starting materials to give $IrClH(Sn^nBu_3)(TFB)(PR_3)$ intermediates similar to **5-7**. Thus the subsequent elimination of $ClSn^nBu_3$ followed by the oxidative addition of a second stannane molecule to $IrH(TFB)(PR_3)$ intermediates should afford **8** and **9** (Scheme 2). A similar mechanism has been previously proposed for the formation of **8** starting from $Ir(XR)(TFB)(PCy_3)$ (X = O, S) and HSn^nBu_3 [7].

Complex **9** was isolated as a white solid and characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. The IR spectrum in Nujol shows a strong absorption at 2071 cm^{-1}, attributable to ν(Ir-H), in agreement with a cis arrangement for these ligands.



Scheme 2.

In the ^1H NMR spectrum in toluene-d_8 the hydrido ligands give rise to a doublet at -16.17 ppm, suggesting that they are equivalent. Near to this resonance the satellites due to the active tin isotopes are observed. With regard to the values of the P-H (21.9 Hz) and Sn-H (82 Hz) coupling constants, there is no doubt that the hydrido ligands are cis disposed to both the phosphine and the stannyl groups. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 29.7 ppm, along with the satellites due to ^{117}Sn and ^{119}Sn isotopes. In accordance with the trans position of the stannyl and phosphine ligands, the values of the P-^{117}Sn and P-^{119}Sn coupling constants are 510 Hz and 534 Hz respectively. Under off-resonance conditions, the singlet is split into a triplet due to the P-H coupling with the two equivalent hydrido ligands.

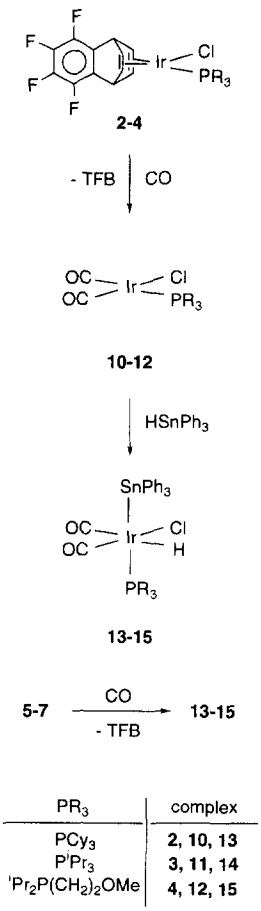
The disposition of ligands around the iridium center of **9** leaves the aliphatic CH protons of the tetrafluorobenzobarrelene diene chemically inequivalent; furthermore, the protons of each carbon-carbon double bond are also mutually inequivalent, although both olefinic bonds are chemically equivalent. As would be expected for this arrangement, the ^1H NMR spectrum of **9** at -80 °C displays two aliphatic resonances at 5.24 and 4.80 ppm and two olefinic signals at 3.25 and 2.51 ppm. However, at room temperature, the spectrum contains only one aliphatic resonance at 4.99 ppm and only one olefinic resonance at 2.92 ppm, suggesting **9** has a rigid structure only at low temperature. At room temperature an intramolecular exchange process takes place which involves the relative positions of the diolefin atoms. A similar fluxional process has been previously observed for **8** [7] and for related dihydrido-silyl complexes [7,14].

2.2. Reactions of $IrCl(CO)_2(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3, $^tPr_2PCH_2CH_2OMe$) with $HSnPh_3$

The tetrafluorobenzobarrelene diolefin of **2-4** can be displaced by carbon monoxide. Thus, the passage of a slow stream of carbon monoxide through dichloromethane solutions of **2-4**, affords the *cis*-di-

carbonyl compounds $IrCl(CO)_2(PR_3)$ ($PR_3 = PCy_3$ (**10**), P^iPr_3 (**11**), $^tPr_2PCH_2CH_2OMe$ (**12**)). In accordance with the mutually cis disposition of both carbonyl ligands, the IR spectra of these compounds show two ν(CO) bands in the terminal carbonyl region.

Similarly to **2-4**, complexes **10-12** react with $HSnPh_3$ by oxidative addition (Scheme 3). Treatment of toluene solutions of **10-12** with 1 equiv. of $HSnPh_3$ leads to the chloro-hydrido complexes $IrClH(SnPh_3)(CO)_2(PR_3)$ ($PR_3 = PCy_3$ (**13**), P^iPr_3 (**14**), $^tPr_2PCH_2CH_2OMe$ (**15**)), which were isolated as white solids in high yield (about 70%). In agreement with the mutually cis disposition of the two carbonyl ligands, the IR spectra of **13-15** have two ν(CO) absorptions between 2061 and 2015 cm^{-1}. The ^1H NMR spectra in benzene-d_6 show at about -7.8 ppm doublets with P-H coupling constants of about 14.5 Hz. The satellites due to the tin isotopes are also observed near to these resonances. The values of the Sn-H coupling constants, between 28 and 46 Hz, strongly support the cis disposition of the triphenylstannyl groups and the hydrido ligands. The $^{31}P\{^1H\}$ NMR spectra contains singlets at 18.0 (**13**), 27.0 (**14**) and 15.4 ppm (**15**) along with the corresponding tin satellites. In agreement with the trans disposition of the phosphine and stannyl ligands, the values of the Sn-P coupling

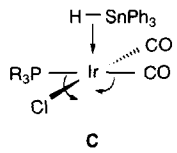


PR_3	complex
PCy_3	**2, 10, 13**
P^iPr_3	**3, 11, 14**
$^tPr_2P(CH_2)_2OMe$	**4, 12, 15**

Scheme 3.

constants are between 990 and 945 Hz. Under off-resonance conditions, the singlets are split into doublets due to the P-H coupling with only one hydrido ligand.

The stereochemistry of **13-15** suggests that the oxidative addition of $HSnPh_3$ to **10-12** occurs along the OC-Ir-P axis with the tin atom above the carbonyl group (**C**). The same approach has been proposed for the oxidative addition of stannanes to the alkynyl complex $Ir(C_2Ph)(CO)_2(PCy_3)$ [7].

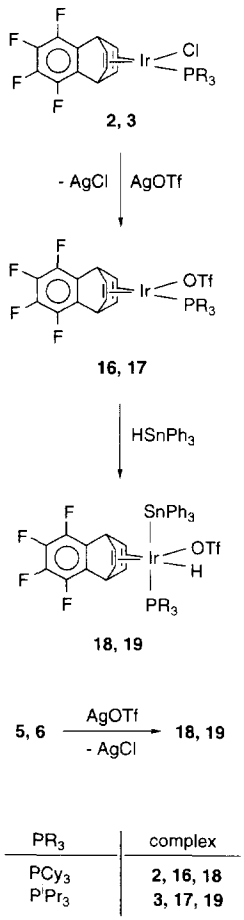


C

Complexes **13-15** can also be obtained in high yield (about 80%) by reaction of **5-7** with carbon monoxide (Scheme 3), suggesting that in these complexes the disposition of the stannyl group is thermodynamically favored. The behavior of **5-7** towards carbon monoxide is similar to that of the alkynyl complex $Ir(C_2Ph)H(SnPh_3)(TFB)(PCy_3)$, which similarly reacts with carbon monoxide to afford $Ir(C_2Ph)H(SnPh_3)(CO)_2(PCy_3)$. However, there is a marked difference between the behavior of these monohydride compounds and the dihydrido complex $IrH_2(SnPh_3)(TFB)(PCy_3)$, which undergoes reductive elimination of molecular hydrogen under carbon monoxide, to finally afford $Ir(SnPh_3)(CO)_3(PCy_3)$ [7]. In contrast to the dihydrido-stannyl, the dihydrido silyl derivatives $IrH_2(SiPh_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3, PPh_3) undergo reductive elimination of silane, to finally give $Ir(\eta^1,\eta^2\text{-}C_{12}F_4H_7)(CO)_2(PR_3)$ by a subsequent insertion of the hydrido ligand into one of the carbon-carbon double bonds of the diene [14].

2.3. Reactions of $Ir(OTf)(TFB)(PR_3)$ ($PR_3 = PCy_3$, P^iPr_3) with $HSnPh_3$

On treatment with AgOTf, the chloro-complexes **2** and **3** give the square-planar derivatives $Ir(OTf)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**16**), P^iPr_3 (**17**)) [9]. The reactions of these compounds with 1 equiv. of $HSnPh_3$ in toluene at room temperature, afford colorless solutions from which the hydrido-stannyl complexes $IrH(OTf)(SnPh_3)(TFB)(PR_3)$ ($PR_3 = PCy_3$ (**18**), P^iPr_3 (**19**)) were isolated in 79% (**18**) and 53% (**19**) yields, as white microcrystalline solids. Complexes **18** and **19** can also be obtained from the reactions of **5** and **6** with AgOTf (Scheme 4), in 85% and 61% yields respectively.



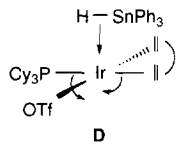
PR_3	complex
PCy_3	**2, 16, 18**
P^iPr_3	**3, 17, 19**

Scheme 4.

The monodentate coordination bonding mode of the trifluoromethanesulfonato anion in these compounds is strongly supported by their IR spectra in KBr, which show bands at 1342 (**18**) and 1324 cm^{-1} (**19**), attributable to the asymmetric $\nu(SO_3)$ vibration [15]. In addition, the spectra contain the ν(Ir-H) absorptions at 2156 (**18**) and 2134 cm^{-1} (**19**), which are displaced by 47 cm^{-1} and 66 cm^{-1} respectively towards low frequency compared with these found for the related chloro-complexes **5** (2203 cm^{-1}) and **6** (2200 cm^{-1}).

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **18** and **19** strongly support the stereochemistry proposed for these compounds in Scheme 4. The ^1H NMR spectra show at -13.20 (**18**) and -12.9 ppm (**19**) doublets along with the satellites due to the active tin isotopes. With regard to the values of the P-H and Sn-H coupling constants, 21.6 and 19.9 Hz (**18**) and 22.5 and 40.1 (**19**) Hz respectively, there is no doubt that in **18** and **19** the hydrido ligand is cis disposed to both the phosphine and stannyl groups. In addition the ^1H NMR spectra contains six resonances between 5.77 and 3.04 ppm for the inequivalent protons of the dienes. The $^{31}P\{^1H\}$ NMR spectra show singlets at -8.8 (**18**) and 3.1 ppm (**19**), which under off-resonance conditions are split into doublets as a result of the P-H coupling with only one hydrido ligand. Near to the singlets the satellites due to the active tin isotopes are also observed. In agreement with the mutually trans disposition of the phosphine and stannyl ligands the values of the ^{117}Sn-P and ^{119}Sn-P coupling constants are 1162 and 1217 Hz (**18**) and 1133 and 1185 (**19**) Hz respectively.

The disposition of ligands around the iridium center for **18** and **19** suggests that, in contrast to the oxidative addition of $HSnPh_3$ to **2-4**, the reactions of **16** and **17** with $HSnPh_3$ take place along the olefin-Ir-P axis, with the tin atom above one of two olefinic bonds of the diene (**D**). As has been previously mentioned, the same approach has been proposed for the addition of $HSnPh_3$ to the alkynyl complex $Ir(C_2Ph)(TFB)(PCy_3)$ (**A**).



D

2.4. The addition of $HSnR_3$ to $IrXL_2(PR_3)$

From these results and those previously reported [6,7], several general trends can be inferred for the reactions of $IrXL_2(PR_3)$ with $HSnR_3$. Thus, we observe that when the L_2 ligand is the tetrafluorobenzobarrelene diolefin, the reaction products can be the dihydrido-stannyl derivatives $IrH_2(SnPh_3)(TFB)(PR_3)$ or the monohydrido-stannyl complexes $IrHX(SnR_3)(TFB)(PR_3)$ depending upon the nature of X and $HSnR_3$. For X = OMe, OEt, O^{i}Pr, OPh and S^{n}Pr, dihydrido-stannyl derivatives are obtained in the presence of $HSnPh_3$ and HSn^nBu_3. The same type of product is formed by treatment of $IrCl(TFB)(PR_3)$ with HSn^nBu_3. However, the additions of $HSnPh_3$ to the above-mentioned square-planar chloro-complexes afford $IrClH(SnPh_3)(TFB)(PR_3)$. Monohydrido-stannyl compounds are also obtained from the oxidative additions of $HSnPh_3$ and HSn^nBu_3 to $Ir(C_2Ph)L_2(PCy_3)$ (L_2 = TFB, 2CO), and from the reactions of $IrCl(CO)_2(PR_3)$ and $Ir(OTf)(TFB)(PR_3)$ with $HSnPh_3$. A particular behavior shows the *cis*-dicarbonyl complex $Ir\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PCy_3)$, which reacts with $HSnPh_3$ to give $Ir(SnPh_3)(CO)_3(PCy_3)$.

The formation of the dihydrido-stannyl derivatives most probably involves the initial oxidative addition of the stannane to the square-planar starting material to afford monohydrido-stannyl intermediates, which by a subsequent reductive elimination of $XSnR_3$ give

$IrH(TFB)(PR_3)$. The oxidative addition of a second molecule of stannane to this intermediate leads to $IrH_2(SnR_3)(TFB)(PR_3)$. The same mechanism has been proposed to the formation of the dihydrido-silyl complexes $IrH_2(SiR_3)L_2(PR_3)$ from $IrXL_2(PR_3)$ and silanes [6,9,16].

In general the approach of the stannane to the square-planar complexes takes place along the olefin-Ir-P axis for the tetrafluorobenzobarrelene starting materials and along the CO-Ir-P axis for the dicarbonyl derivatives. In both cases, the hydrogen atom is cis disposed to the phosphorus. However, the stereochemistry of the complexes $IrClH(SnPh_3)(TFB)(PR_3)$, with the hydrido and the stannyl group trans disposed to the chlorine and diene respectively, suggest that the additions of $HSnPh_3$ to $IrCl(TFB)(PR_3)$ occur via an olefin-Ir-Cl orientation with the hydrogen atom above one of the two carbon-carbon double bonds of the diene.

In conclusion, the reaction products (and their stereochemistry) from the oxidative addition of $HSnR_3$ to square-planar $IrXL_2(PR_3)$ complexes (L_2 = TFB, 2CO) depend upon the nature of X, L_2 and $HSnR_3$, and are independent of the phosphine ligand.

3. Experimental details

3.1. General considerations

All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $IrCl(TFB)_2$ [17], $IrCl(TFB)(PR_3)$ ($PR_3 = PCy_3$ and P^iPr_3 [9]) and $Ir(OTf)(TFB)(PR_3)$ ($R = PCy_3$ and P^iPr_3 [9]) were prepared by published methods. The NMR spectra were recorded on a Varian UNITY 300 or on a Bruker 300 ARX instruments and the IR spectra on a Perkin Elmer 783 spectrometer. C, H and S analyses were carried out with a Perkin Elmer 2400 CHNS/O microanalyzer.

3.2. Preparation of $IrCl(TFB)(\kappa P\text{-}^iPr_2PCH_2CH_2OMe)$ (4)

This compound was prepared from $IrCl(TFB)_2$ (102.0 mg, 0.150 mmol) and $^iPr_2PCH_2CH_2OMe$ (31 μl, 0.160 mmol) by a procedure similar to that published for **2,3** [9] (yield, 81 mg (86%)). Anal. Found: C, 39.75; H, 4.51. $C_{21}H_{27}ClF_4IrOP$ calc.: C, 40.04; H, 4.32%. IR (Nujol): ν(IrCl) 317 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 4.87 (br, 2H, -CH), 3.87 (br, 2H, =CH), 3.18 (m, 2H, OCH_2), 2.83 (s, 3H, OCH_3), 1.85 (m, 2H, $PCHCH_3$), 1.62 (br, 2H, =CH), 1.52 (m, 2H, PCH_2), 0.98 (dd, 6H, J(HH) = 7.1 Hz, J(PH) = 15.6 Hz, $PCHCH_3$), 0.76 (dd, 6H, J(HH) = 7.1 Hz, J(PH) = 14.3 Hz, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 20.3 (s).

3.3. Preparation of $IrClH(SnPh_3)(TFB)(PCy_3)$ (5)

A solution of **2** (100.0 mg, 0.136 mmol) in 7 ml of toluene was treated with $HSnPh_3$ (47.8 mg, 0.136 mmol). The orange solution became pale yellow upon addition of the reagent. The solvent was removed and the residue was treated with 5 ml of pentane to give a white microcrystalline solid. The solution was decanted and the solid was repeatedly washed with pentane and dried in vacuo (yield, 125 mg (85%)). Anal. Found: C, 53.03; H, 4.74. $C_{48}H_{55}ClF_4IrPSn$ calc.: C, 53.12; H, 5.11%. IR (Nujol): ν(IrH) 2203, ν(IrCl) 320, ν(SnPh) 259 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 8.10-7.13 (m, 15H, Ph), 5.79 (br, 1H, -CH), 4.92 (br, 1H, -CH), 4.64 (br, 1H, =CH), 4.35 (br, 1H, =CH), 4.06 (br, 2H, =CH), 2.00-0.92 (m, 33H, PCy_3), -16.26 (d with tin satellites, 1H, J(PH) = 17.4 Hz, J(SnH) = 21.3 Hz, Ir-H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 145.0 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 90 Hz, C_{ipso} $SnPh_3$), 136.0 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 49 Hz, $SnPh_3$), 130.3 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 15 Hz, $SnPh_3$), 129.0 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 65 Hz, $SnPh_3$), 77.4 (d, J(PC) = 13.9 Hz, =CH), 68.7 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 86 Hz, =CH), 65.6 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 52 Hz, =CH), 63.9 (d, J(PC) = 8.1 Hz, =CH), 41.4 (s, -CH), 39.6 (s, PCy_3), 37.4 (d, J(PC) = 26.5 Hz, PCy_3), 35.4 (s, -CH), 29.8 (d, J(PC) = 15.6 Hz, PCy_3), 26.9 (s, PCy_3), 26.2 (s, PCy_3). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ -3.9 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 84.8 Hz; doublet in off-resonance).

3.4. Preparation of $IrClH(SnPh_3)(TFB)(P^iPr_3)$ (6)

This compound was prepared as described for **5**, using **3** (83.5 mg, 0.136 mmol) and $HSnPh_3$ (47.8 mg, 0.136 mmol) as starting materials. A white solid was obtained (yield, 115 mg (88%)). Anal. Found: C, 48.30; H, 4.52. $C_{39}H_{43}ClF_4IrPSn$ calc.: C, 48.54; H, 4.49%. IR (Nujol): ν(IrH) 2200, ν(IrCl) 320, ν(SnPh) 265 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.70-7.24 (m, 15H, Ph), 5.72, 5.21 (both br, 1H each, -CH), 4.76, 4.58, 4.23, 3.97 (all br, 1H each, =CH), 2.00 (m, 3H, $PCHCH_3$), 1.18 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, $PCHCH_3$), 1.11 (dd, 9H, J(HH) = 6.9 Hz, J(PH) = 13.8 Hz, $PCHCH_3$), -16.77 (d with tin satellites, 1H, J(PH) = 18.0 Hz, J(SnH) = 42.0 Hz, Ir-H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 144.1 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 87 Hz, C_{ipso} $SnPh_3$), 136.1 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 48 Hz, $SnPh_3$), 130.5 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 14 Hz, $SnPh_3$), 129.1 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 64 Hz, $SnPh_3$), 77.2 (d, J(PC) = 14.2 Hz, =CH), 69.7 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 85 Hz, =CH), 65.6 (s with tin satellites, $J(P\text{-}^{117/119}Sn)$ = 50 Hz, =CH), 63.7 (d, J(PC) =

7.3 Hz, =CH), 41.4 (s, -CH), 35.6 (s, -CH), 27.9 (d, J(PC) = 28.5 Hz, PCHCH$_3$), 19.9 (s, PCHCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 6.7 (s with tin satellites, J(P-$^{117/119}$Sn) = 84.3 Hz; doublet in off-resonance).

3.5. Preparation of IrClH(SnPh$_3$)(TFB)(κP-^{i}Pr$_2$PCH$_2$CH$_2$OMe) (7)

This compound was prepared as described for **5**, using **4** (85.7 mg, 0.136 mmol) and HSnPh$_3$ (47.8 mg, 0.136 mmol) as starting materials. A white solid was obtained (yield, 76 mg (57%)). Anal. Found: C, 48.02; H, 4.51. $C_{39}H_{43}ClF_4IrOPSn$ calc.: C, 47.75; H, 4.42%. IR (Nujol): ν(IrH) 2205, ν(IrCl) 320, ν(SnPh) 255 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 8.15-7.20 (m, 15H, Ph), 5.63, 4.74 (both br, 1H each, -CH), 4.53, 4.29, 3.48, 3.43 (all br, 1H each, =CH), 2.92 (m, 4H, OCH$_2$ and PCH$_2$), 2.71 (s, 3H, OCH$_3$), 1.95 (m, 2H, PCHCH$_3$), 1.24 (dd, 3H, J(HH) = 6.8 Hz, J(PH) = 14.6 Hz, PCHCH_3), 0.92 (dd, 3H, J(HH) = 6.5 Hz, J(PH) = 16.4 Hz, PCHCH_3), 0.86 (dd, 3H, J(HH) = 6.5 Hz, J(PH) = 13.2 Hz, PCHCH_3), 0.73 (dd, 3H, J(HH) = 6.9 Hz, J(PH) = 12.7 Hz, PCHCH_3), -16.42 (d with tin satellites, 1H, J(PH) = 16.2 Hz, J(SnH) = 55.1 Hz, Ir-H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 9.1 (s with tin satellites, J(P-$^{117/119}$Sn) = 84.3 Hz; doublet in off-resonance).

3.6. Preparation of IrH$_2$(Sn^{n}Bu$_3$)(TFB)(P^{i}Pr$_3$) (9)

This compound was prepared from **4** (83.5 mg, 0.136 mmol) and HSn^{n}Bu$_3$ (36 μl, 0.136 mmol) by a procedure similar to that published for **8** [7] (yield, 41 mg (35%)). Anal. Found: C, 45.42; H, 6.15. $C_{33}H_{56}F_4IrPSn$ calc.: C, 45.52; H, 6.48%. IR (Nujol): ν(IrH) 2071, ν(SnPh) 260 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 4.99 (br, 2H, -CH), 2.92 (br, 4H, =CH), 1.56 (m, 3H, PCHCH$_3$), 1.81, 1.57, 1.38 (all m, 6H each, Sn(CH$_2$)$_3$), 1.05 (m, 9H, Sn(CH$_2$)$_3$CH_3), 0.90 (dd, 18H, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, PCHCH_3), -16.17 (d with tin satellites, 2H, J(PH) = 21.9 Hz, J(SnH) = 82.5 Hz, Ir-H). ^{1}H NMR (300 MHz, C_7D_8, -80 °C): δ 5.24, 4.80 (both br, 1H each, -CH), 3.25, 2.51 (both br, 2H each, =CH), the other resonances are the same as that at 20 °C. ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 29.7 (s with tin satellites, J(P-^{119}Sn) = 534.4 Hz, J(P-^{117}Sn) = 510.3 Hz; triplet in off-resonance).

3.7. Preparation of IrCl(CO)$_2$(PCy$_3$) (10)

A solution of **2** (100.0 mg, 0.136 mmol) in 8 ml of CH_2Cl_2 was stirred under CO for 10 min. A change from orange to lemon yellow was observed. The solution was concentrated under reduced pressure to 0.5 ml. Hexane was added, and the solution was cooled to -20 °C over 24 h, causing the precipitation of a yellow solid, which was decanted, washed with hexane, and dried in vacuo (yield, 54 mg (70%)). Anal. Found: C, 42.48; H, 6.06. $C_{20}H_{33}ClIrO_2P$ calc.: C, 42.58; H, 5.90%. IR (Nujol): ν(CO) 2062, 1986 cm^{-1}. IR (CH_2Cl_2): ν(CO) 2072, 1984 cm^{-1}. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$): δ 29.0 (s).

3.8. Preparation of IrCl(CO)$_2$(P^{i}Pr$_3$) (11)

A solution of **3** (83.5 mg, 0.136 mmol) in 10 ml of CH_2Cl_2 was stirred under CO for 5 min. A change from orange to lemon yellow was observed. The solvent was removed and the residue was washed with cold hexane to give a pale yellow oil. IR (CH_2Cl_2): ν(CO) 2077, 1986 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.76 (m, 3H, PCHCH$_3$), 1.36 (dd, 18H, J(HH) = 7.2 Hz, J(PH) = 14.7 Hz, PCHCH_3). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$): δ 39.4 (s).

3.9. Preparation of IrCl(CO)$_2$(κP-^{i}Pr$_2$PCH$_2$CH$_2$OMe) (12)

This compound was prepared as described for **11**, using **4** (85.7 mg, 0.136 mmol) as starting material. A light yellow oil was obtained. IR (CH_2Cl_2): ν(CO) 2072, 1983 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.54 (m, 2H, OCH$_2$), 3.02 (s, 3H, OCH$_3$), 2.19-2.07 (m, 4H, PCH$_2$ and PCHCH$_3$), 1.05 (dd, 6H, J(HH) = 7.2 Hz, J(PH) = 16.2 Hz, PCHCH_3), 0.94 (dd, 6H, J(HH) = 7.1 Hz, J(PH) = 15.1 Hz, PCHCH_3). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$): δ 31.9 (s).

3.10. Preparation of IrClH(SnPh$_3$)(CO)$_2$(PCy$_3$) (13)

A solution of **10** (100 mg, 0.177 mmol) in 10 ml of CH_2Cl_2 was treated with HSnPh$_3$ (62 mg, 0.177 mmol). The resulting pale yellow solution was concentrated to ca. 0.5 ml, and addition of hexane precipitated a white solid. The solution was decanted, and the solid was repeatedly washed with hexane and dried in vacuo (yield, 120 mg (74%)). Anal. Found: C, 50.11; H, 5.45. $C_{38}H_{49}ClIrO_2PSn$ calc.: C, 49.87; H, 5.40%. IR (Nujol): ν(IrH) 2125, ν(CO) 2050, 2015 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 8.10-7.18 (m, 15H, Ph), 2.08-1.10 (m, 33H, PCy$_3$), -7.65 (d with tin satellites, 1H, J(PH) = 14.5 Hz, J(SnH) = 28.2 Hz, Ir-H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 18.0 (s with tin satellites, J(P-^{119}Sn) = 989.1 Hz, J(P-^{117}Sn) = 944.5 Hz; doublet in off-resonance).

This complex can also be prepared from **5** (100.0 mg, 0.090 mmol) in CH_2Cl_2 under CO atmosphere for 30 min (yield, 59 mg (70%)).

3.11. Preparation of $IrClH(SnPh_3)(CO)_2(P^iPr_3)$ (14)

This compound was prepared as described for **13**, using **11** (46.1 mg, 0.104 mmol) and $HSnPh_3$ (36.4 mg, 0.104 mmol) as starting materials (yield, 63 mg (76%)). **14** can also be obtained from **6** (131 mg, 0.136 mmol) and an atmosphere of CO (yield, 93 mg (86%)). Anal. Found: C, 43.91; H, 4.83. $C_{29}H_{37}ClIrO_2PSn$ calc.: C, 43.82; H, 4.69%. IR (Nujol): ν(IrH) 2136, ν(CO) 2061, 2020 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 8.00-7.03 (m, 15H, Ph), 1.88 (m, 3H, PC$H$$CH_3$), 0.72 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 14.1 Hz, PCHCH_3), 0.68 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 14.7 Hz, PCHCH_3), -7.96 (d with tin satellites, 1H, J(PH) = 14.1 Hz, J(SnH) = 29.1 Hz, Ir-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 27.0 (s with tin satellites, J(P-^{119}Sn) = 990.0 Hz, J(P-^{117}Sn) = 946.6 Hz; doublet in off-resonance).

3.12. Preparation of $IrClH(SnPh_3)(CO)_2(\kappa P$-$^iPr_2PCH_2CH_2OMe)$ (15)

This compound was prepared as described for **13**, using **7** (133 mg, 0.136 mmol) and an atmosphere of CO as starting materials (yield, 80 mg (73%)). **15** can also be obtained from **12** (47.8 mg, 0.104 mmol) and $HSnPh_3$ (36.4 mg, 0.104 mmol) (yield, 63 mg (67%)). Anal. Found: C, 42.50; H, 4.13. $C_{29}H_{37}ClIrO_3PSn$ calc.: C, 42.95; H, 4.60%. IR (Nujol): ν(IrH) 2138, ν(CO) 2059, 2023 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 8.16-7.18 (m, 15H, Ph), 3.30 (m, 2H, OCH_2), 2.93 (s, 3H, OCH_3), 1.99-1.67 (m, 4H, PCH_2 and PC$H$$CH_3$), 0.92-0.70 (m, 12H, PCHCH_3), -7.96 (d with tin satellites, 1H, J(PH) = 14.7 Hz, J(SnH) = 45.7 Hz, Ir-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 15.4 (s with tin satellites, J(P-$^{119/117}$Sn) = 975.1 Hz; doublet in off-resonance).

3.13. Preparation of $IrH(OTf)(SnPh_3)(TFB)(PCy_3)$ (18)

To a solution of **16** (150.0 mg, 0.177 mmol) in 10 ml of toluene was added $HSnPh_3$ (62 mg, 0.177 mmol). After stirring for 1 h the solvent was removed and the residue was treated with 5 ml of pentane to give a white microcrystalline solid. The solution was decanted and the solid was repeatedly washed with pentane and dried in vacuo (yield, 168 mg (79%)). Anal. Found: C, 49.20; H, 4.70; S, 2.75. $C_{49}H_{55}F_7IrO_3PSSn$ calc.: C, 49.09; H, 4.62; S, 2.67%. IR (KBr): ν(IrH) 2156, $\nu(SO_3)$ 1342, ν(SnPh) 262 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.80-6.5 (m, 15H, Ph), 5.43, 5.08 (both br, 1H each, -CH), 4.72, 3.83, 3.49, 3.32 (all br, 1H each, =CH), 2.20-1.10 (m, 33H, PCy_3), -13.20 (d with tin satellites, 1H, J(PH) = 21.6 Hz, J(SnH) = 19.9 Hz, Ir-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ-8.8 (s with tin satellites, J(P-^{119}Sn) = 1217.4 Hz, J(P-^{117}Sn) = 1162.5 Hz; doublet in off-resonance). ^{19}F NMR (282.3 MHz, $CDCl_3$): δ-78.6 (s).

This complex can also be prepared from **5** (100.0 mg, 0.092 mmol) and AgOTf (23.7 mg, 0.092 mmol) as starting materials (yield, 94 mg (85%)).

3.14. Preparation of $IrH(OTf)(SnPh_3)(TFB)(P^iPr_3)$ (19)

This compound was prepared as described for **18**, using **17** (75.7 mg, 0.104 mmol) and $HSnPh_3$ (36.4 mg, 0.104 mmol) (yield, 59 mg (53%)). **19** can also be obtained from **6** (131 mg, 0.136 mmol) and AgOTf (35.0 mg, 0.092 mmol) as starting materials (yield, 89 mg (61%)). Anal. Found: C, 44.49; H, 4.21; S, 3.14. $C_{40}H_{43}F_7IrO_3PSSn$ calc.: C, 44.54; H, 4.02; S, 2.97%. IR (KBr): ν(IrH) 2134, $\nu(SO_3)$ 1324, ν(SnPh) 261 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.00-7.1 (m, 15H, Ph), 5.77, 5.70 (both br, 1H each, -CH), 5.09, 4.76, 3.08, 3.04 (all br, 1H each, =CH), 1.99 (m, 3H, PC$H$$CH_3$), 0.93 (dd, 6H, J(HH) = 7.0 Hz, J(PH) = 13.2 Hz, PCHCH_3), 0.51 (dd, 6H, J(HH) = 6.9 Hz, J(PH) = 13.7 Hz, PCHCH_3), -12.9 (d with tin satellites, 1H, J(PH) = 22.5 Hz, J(SnH) = 40.1 Hz, Ir-H). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 3.1 (s with tin satellites, J(P-^{119}Sn) = 1184.6 Hz, J(P-^{117}Sn) = 1132.8 Hz; doublet in off resonance). ^{19}F NMR (282.3 MHz, $CDCl_3$): δ-78.6 (s).

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