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(2-STANNYLATED BUTADIENE) TRICARBONYL IRON COMPLEXES : PRACTICAL REAGENTS FOR THE SYNTHESIS OF 2-ACYLDIENES

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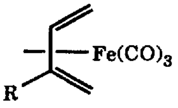
SUMMARY: *A new route to the stable (2-acylbutadiene) tricarbonyl iron complexes is described, based on the palladium catalyzed coupling between acid chlorides and 2-stannylated butadiene complexes .*

Conjugated dienes bearing an electron-withdrawing group in position 2 are very reactive derivatives which are difficult to isolate as monomers, especially in the case of the parent 2-substituted butadienes. These functionalized isoprenes form however stable tricarbonyl iron complexes (1). Unfortunately complexes of the type I with R = CHO or COR' are not accessible by electrophilic functionalization of (butadiene) tricarbonyl iron. This complex and complexes of simply alkylated butadienes are in fact readily acylated in the 1 or 4 position under Friedel-Crafts conditions (2). To our knowledge, access to 2-acyldienes via a Friedel-Crafts reaction of carbonyl iron complexes is limited to the acylation of (tetramethylallene) tetracarbonyl iron (3) and (butadiene) hexacarbonyl diiron (4) complexes .

We therefore investigated the possibility of an ipso-substitution of 2-silylated butadiene complexes under the conditions of the Friedel-Crafts reaction. Although well documented for simple vinylsilanes, this reaction did not work in our case. The substitution of the silyl substituent seems to be impossible to perform and again only linear dienone complexes were obtained (5). Under more drastic conditions or by repetition of the reaction a second unprecedented terminal acylation was observed ("1,4-bisacylation"), the silicon remaining unaffected (6).

Herein, we describe an approach which is not based on a Friedel-Crafts reaction. This novel and short route to 2-acylbutadiene complexes relies upon a coupling reaction between acid chlorides and 2-stannylated butadiene complexes, catalyzed by palladium derivatives. The palladium catalyzed coupling reaction of acid chlorides with organostannanes is a general reaction (7), and is seen to be efficient even with the unusual organostannanes used here.

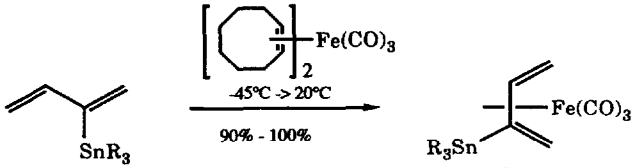
The starting complexes **1a** and **1b** (8) were synthesized in quantitative yields by ligand exchange between 2-stannylated butadiene (9) and (biscyclooctene) tricarbonyl iron -Grevels'reagent- (10). More classical methods of complexation, such as irradiation of pentacarbonyl iron or heating nonacarbonyl diiron in presence of the diene, afford the desired complexes in only low to modest yields.



I

R = CO_2H, CO_2R'

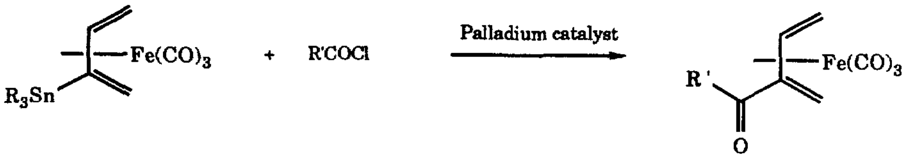
CHO, COR'



1a (R = nBu)

1b (R = Me)

The coupling of these stannylated complexes with different acid chlorides was found to be very dependent on the experimental conditions (temperature, solvent, catalyst, atmosphere) as shown in the table.



1a , 1b   Palladium catalyst : $Pd(PPh_3)_4$ or $PdClBn(PPh_3)_2$ 2 - 7

TABLE

R	S.M.	R'	Solvent	T °C (h)	Yield	Product
1	1a	Me	THF	60 (20)	0 %	-
2	1a	Et	HMPA	60 (20)	0 %	2
3	1a	Et	$HCCl_3$	60 (20)	60 %	2
4	1a	Et	$(CH_2Cl)_2$	80 (4)	60 %	2
5	1a	Me	$(CH_2Cl)_2$	50 (20)	40 %	3
6	1a	iPr	$(CH_2Cl)_2$	80 (4)	17 %	4
7	1a	iPr	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	48 %	4
8	1a	phenyl	$(CH_2Cl)_2$	80 (4)	23 %	5
9	1a	phenyl	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	43 %	5
10	1a	$CH_3CH{=}CH$	$(CH_2Cl)_2$	80 (4)	31 %	6
11	1a	$CH_3CH{=}CH$	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	38 %	6
12	1b	Et	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	70 %	2
13	1b	Me	$(CH_2Cl)_2$ / 20 % HMPA	50 (24)	66 %	3
14	1b	iPr	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	58 %	4
15	1b	phenyl	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	90 %	5
16	1b	$CH_3CH{=}CH$	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	51 %	6
17	1b	$EtO_2C(CH_2)_2$	$(CH_2Cl)_2$ / 20 % HMPA	80 (2)	60 %	7

For example, refluxing stoichiometric quantities of **1a** and acetyl chloride in THF in the presence of a catalytic amount of $Pd(PPh_3)_4$ for 20 hours, led to the recovery of starting material and destannylated butadiene complex (run 1). Heating **1a** and propionyl chloride in HMPA in the presence of $Pd(PPh_3)_4$ or $PdBnCl(PPh_3)_2$ gave only traces of the acylated product **2** (run 2). However, **1a** and propionyl chloride gave the desired acylated complex **2** (run 3), when heated in refluxing chloroform for 20 hours with catalytic amount of $PdBnCl(PPh_3)_2$ (this catalyst was used throughout all the other runs) . A comparable yield was also obtained when the same mixture of compounds was heated in refluxing 1,2-dichloroethane as solvent for only 4 hours (run 4) .Adding HMPA (20% by volume) to the reaction mixture and decreasing the reaction time led to higher yields by 10-20% (runs 7,9,11). Finally, it was found that 2-trimethylstannyl butadiene complex **1b** afforded better yields than the tributyltin complex **1a** (runs 12-17).

Both simple acid chlorides and functionalized ones could be used since the coupling reaction is compatible with different functional groups such as double bonds, aryls or esters (runs 8-11 and 15-17).

*Typical procedure: In an argon filled two necked flask equiped with a condenser and a bubbler, benzylchlorobistriphenylphosphine palladium (20 mg; 0.026 mmole) and propionyl chloride (0.13 ml;140 mg; 1.5 mmoles) are dissolved in 1,2-dichloroethane (2.5 ml). A solution of (2-trimethylstannylbutadiene) tricarbonyl iron **1b** (358 mg; 1 mmole) in dichloroethane (1.5 ml) and HMPA (1 ml) is added via syringe. The mixture is refluxed for 2 hours and then cooled to room temperature. The solution is taken up in 50 ml of a mixture of ether and hexane (50:50), washed with water (4x50 ml), dried over $MgSO_4$,filtered and concentrated under reduced pressure. The crude product is chromatographed on a silica gel column eluting with hexane/ether (95:5) to give complex **2** (176 mg) in 70 % yield (11).*

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5. Even 1-silylated butadiene complexes do not undergo silicon ipso-subsitution, unless there is an alkyl group in the 4 position, see:
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8. Complex **1b**: yellow liquid ; NMR (200MHz, $CDCl_3$) : 0.30 ppm (9H, m, J Sn-H = 55.4 Hz , 53.0 Hz), 0.45 ppm (1H, dd, J = 2.0 Hz, 1.0 Hz), 0.60 ppm (1H, dd, J = 9.3 Hz, 2.1 Hz), 1.78 ppm (1H, dd, J = 2.0Hz, 1.0 Hz), 1.98 ppm (1H, dd, J = 6.7 Hz, 2.1 Hz), 5.11 ppm (1H, m, J = 9.3 Hz, 6.7 Hz, 1.0 Hz, 1.0 Hz) ; IR (CCl_4) : ν (C≡O) = 1970, 1980 , 2040 cm^{-1} ; analyses : - calcd. for $C_{10}H_{14}FeO_3Sn$ %C : 33.66, H : 3.95 - found %C : 34.0, H : 3.9.

9. 2-stannylated butadienes were obtained from 2-chloroprene according to :
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11. Complex **2** : yellow crystals, m.p. 28-29°C ; NMR (200MHz, $CDCl_3$) : 0.22 ppm (1H, dd, J = 2.9 Hz , 0.7 Hz), 0.56 ppm (1H, dd, J = 9.9 Hz, 2.0 Hz), 1.22 ppm (3H, t, J = 7.3 Hz), 2.06 ppm (1H, dd, J = 7.0 Hz, 2.0 Hz), 2.39 ppm (1H, dd, J = 2.9 Hz, 1.6 Hz), 2.80 ppm (2H, m), 6.17 ppm (1H, m, J = 9.9 Hz, 7.0 Hz, 1.6 Hz, 0.7 Hz) ; IR (CCl_4) : ν (C=O) = 1690cm^{-1}, ν (C≡O) = 1980, 1990 , 2050 cm^{-1} ; analyses : - calcd.for $C_{10}H_{11}FeO_4$ %C : 48.04, H : 4.43 - found %C : 48.0, H : 4.0.

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