Intervention by an η^6-Organochromium Moiety Switches Chemoselectivity in Palladium-Catalyzed Reactions with Trialkyltin Compounds

Damien Prim, Jean-Philippe Tranchier, René Chavignon, Françoise Rose-Munch, and Eric Rose*

Laboratoire de Synthèse Organique et Organométallique, UMR CNRS 7611, Université Pierre et Marie Curie, Tour 44-1er étage, 4, Place Jussieu, 75252 Paris Cedex 05, France

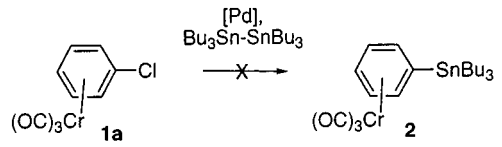
Received January 2, 2001

Summary: The reaction of (chloroarene)tricarbonylchromium with hexaalkylditin under palladium catalysis does not proceed by the expected Stille reaction with addition of an SnR_3 group but, instead, affords alkylarene complexes via a postulated chromium-assisted alkyl migration.

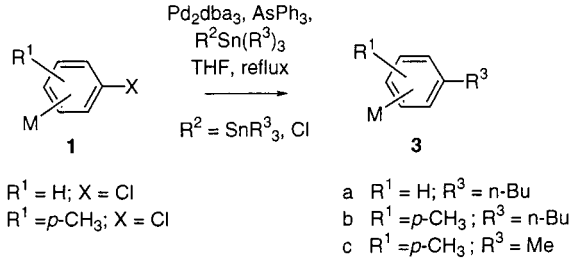
Trialkylaryltin derivatives have found widespread applications in organic synthesis in the last two decades,[1] and palladium-catalyzed coupling reactions using such compounds constitute the popular and general Stille coupling procedure.[2] The combination of the organotin coupling procedure with chromium-bound π-systems is, however, far less fully explored. In an attempt to prepare (η^6-phenyl)trialkyltin compounds for use in our continuing studies of tricarbonylchromium arene complexes[3] in palladium-catalyzed cross-coupling reactions,[4] we have examined the transfer of trialkyltin to (η^6-chlorobenzene)tricarbonylchromium derivatives.

Attempts to prepare the tributyltin(η^6-benzene)tricarbonylchromium complex **2** from the (η^6-chlorobenzene)tricarbonylchromium complex **1**, using hexabutylditin together with $Pd_2(dba)_3$ and $AsPh_3$ as catalyst in refluxing THF, failed. The expected product of the Stille reaction complex **2**, which corresponds to the stannylation of the arene, was not formed (Scheme 1). Instead, (η^6-butylbenzene)$Cr(CO)_3$ (**3a**) was isolated in high yield as the sole product, indicating an overall displacement of the chloride by the butyl group (Scheme 2). Alkyl transfer from hexaalkylditin is, as far as we are aware, unprecedented, whereas alkyl transfer from tetraalkyltin to arylhalides (or triflates) under palladium catalysis is well-known.[5] We wish to report here the initial study of this unexpected palladium-catalyzed reaction.

Scheme 1



Scheme 2



Results of our investigations are listed in Table 1. (η^6-Chlorobenzene)tricarbonylchromium (**1a**) reacted with Sn_2Bu_6, $AsPh_3$, and $Pd_2(dba)_3$, giving rise to the formation of butyl derivative **3a** in 88% yield (entry 1). When the above reaction conditions were applied to the free bromobenzene, no alkyl transfer product **3a** was detected (entry 2), but in contrast, 1,1′-biphenyl resulting from a homocoupling reaction[6] could be isolated in 34% yield together with 10% of unreacted starting material. The noncomplexed *p*-nitrochlorobenzene gave no reaction, and it was recovered unchanged (entry 3). This result demonstrated that the electron deficiency in the nitroarene ring (which is comparable to the arene $Cr(CO)_3$ ring) was not alone sufficient to promote the unusual alkyl transfer reaction, suggesting that the chromium entity could be directly involved in the alkyl migration.

The generality of the alkyl transfer reaction was examined with disubstituted chloroarene complexes. (η^6-*p*-Chlorotoluene)tricarbonylchromium (**1b**) reacted with

* To whom correspondence should be addressed. E-mail: rose@ccr.jussieu.fr.

(1) See for example: (a) Corsico, E. F.; Rossi, R. A. *Synlett* **2000**, *2*, 230. (b) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2411. (c) Borzilleri, R. M.; Weinreb, S. M. *J. Am. Chem. Soc.* **1994**, *116*, 9789. (d) Nicolaou, K. C.; Chakraborty, T. K.; Piscopo, A. D.; Minowa, N.; Bertinato, P. *J. Am. Chem. Soc.* **1993**, *115*, 4419. (e) Pattenden, G.; Thom, S. M. *Synlett* **1993**, 215.

(2) (a) Han, X.; Stoltz, B. M.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 7600. (b) Casado, A. L.; Espinet, P. *J. Am. Chem. Soc.* **1998**, *120*, 8978. (c) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954. (d) Farina, V.; Krishnarmurthy, V.; Scott, J. The Stille Reaction. In *Organic Reactions*; Paquette, L. A., Ed.; Wiley: Chichester, U.K., 1997; Vol. 50, pp 1−633. (e) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905. (f) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(3) (a) Rose-Munch, F.; Rose, E.; Djukic, J. P.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, 1295. (b) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445. (c) Rose-Munch, F.; Gagliardini, V.; Renard, C.; Rose, E. *Coord. Chem. Rev.* **1998**, *178−180*, 249.

(4) (a) Prim, D.; Tranchier, J.-P.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, *5*, 901. (b) Tranchier, J−P.; Chavignon, R.; Prim, D.; Auffrant, A.; Plyta, Z. F.; Rose-Munch, F.; Rose, E. *Tetrahedron Lett.* **2000**, *41*, 3607. (c) Prim, D.; Kirsch, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2603.

(5) (a) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, R. P. *J. Org. Chem.* **1993**, *58*, 5434. (b) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (c) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(6) Homocoupling was already observed in high yield using Stille conditions. See for example ref 5c.

10.1021/om010004s CCC: $20.00
Publication on Web 03/09/2001

Table 1. Stille Coupling Reactions of Complexes 1

entry	R^1	M	X	$R^2SnR^3_3$ (1 equiv)	catalyst (0.05 equiv, 0.2 equiv)	conditions	1	3
1	H	$Cr(CO)_3$	Cl	$(Bu_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 3 h		88
2	H		Br	$(Bu_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 2 h	10[a]	
3	NO_2		Cl	$(Bu_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 2 h	100	
4	Me	$Cr(CO)_3$	Cl	$(Bu_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 2 h		75
5	Me	$Cr(CO)_3$	Cl	Bu_3SnCl	Pd_2dba_3, $AsPh_3$	THF, reflux, 2 h		85
6	Me	$Cr(CO)_3$	Cl	$(Bu_3Sn)_2$		THF, reflux, 2 h	100	
7	Me	$Cr(CO)_3$	Cl	$(Bu_3Sn)_2$	$Pd(TPP)_4$	THF, reflux, 5 h	100	
8	Me	$Cr(CO)_3$	Cl	$(Bu_3Sn)_2$	Pd_2dba_3, dppf	THF, reflux, 5 h	100	
9	Me	$Cr(CO)_3$	Cl	Bu_4Sn	Pd_2dba_3, $AsPh_3$	THF, reflux, 2 h		81
10	Me	$Cr(CO)_3$	Cl	$(Me_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 3 h	22	68
11	Me	$Cr(CO)_3$	F	$(Bu_3Sn)_2$	Pd_2dba_3, $AsPh_3$	THF, reflux, 3 h	100	
12	H	$Cr(CO)_3$	Cl	2	Pd_2dba_3, $AsPh_3$	THF, reflux, 18 h	100	

[a] 34% homocoupling product.

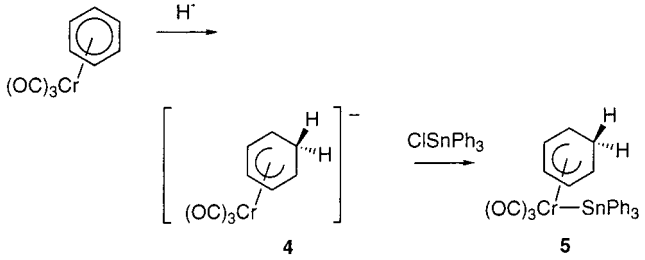
hexabutylditin to afford the corresponding butyl-substituted complex **3b** in 75% yield (entry 4). The formation of *p*-*n*-butyltoluene complex confirmed the regioselectivity of this reaction. The butyl transfer resulted from an overall *ipso* substitution of the chlorine atom. In the same way, the butyl transfer occurred in 85% yield by using Bu_3SnCl as the reactant (entry 5). An attempted reaction without the catalytic system under the same conditions (THF, reflux) gave no coupling product, and the starting complex was recovered unchanged (entry 6). This clearly confirmed that butyl transfer is a result of a Pd-catalyzed process.

Moreover, the use of neither triphenylphosphine (TPP; entry 7) nor bidentate diphenylphosphinoferrocene (dppf; entry 8) in refluxing THF for 5 h afforded coupling products. Thus, we observed this reaction only in the presence of $AsPh_3$ as ligand. The role of $AsPh_3$ has been studied by Farina,[5] and the compound has been introduced in Stille coupling reactions because of its high nucleophilicity, which allows fast transmetalation steps. We recently stressed its high potentiality in cross-coupling reactions involving (η^6-arene)tricarbonylchromium complexes by allowing milder reaction conditions and by avoiding side reactions,[4a] but no satisfying explanation for the exact role of this ligand has been yet found.

The known alkyl transfer using tetrabutyltin[7] afforded similar yields (81%) under the aforementioned conditions (entry 9). The alkyl transfer process was then extended to a methyl migration in the case of hexamethylditin (entry 10). Although the *p*-xylene complex **3c** was obtained in 68% yield, hexamethylditin appeared less reactive than the butyl analogue at comparable reaction times. It is noteworthy that only chloroarene complexes undergo alkyl transfer; indeed in the case of fluoro derivatives[8] no alkyl migration was observed and starting material was recovered unchanged (entry 11).

Trialkyltin arenes are the expected products of palladium-catalyzed reactions of hexaalkylditin and aryl halides;[9] thus, one could expect the formation of such an intermediate in the first step and subsequent metal-catalyzed rearrangement of the latter to afford the butylarene complex **3**. For this purpose, we prepared tributyltinarene complex **2** by trapping the lithio derivative $C_6H_5LiCr(CO)_3$ with $ClSnBu_3$. We then reacted

Scheme 3



this η^6-tributyltin benzene complex **2** with the chloro derivative **1a** under the alkyl transfer reaction conditions mentioned above, at room temperature for 24 h or at reflux for 18 h (entry 12), but we did not observe the formation of either the complex **3a** or the binuclear biphenyl complex $[C_6H_5Cr(CO)_3]_2$ which could also be expected; complex **2** was recovered unchanged. From this result it is clear that a trialkyltin arene complex such as **2** cannot be an intermediate in the alkyl transfer process.[10]

When these data are taken into account, it is obvious that, besides the activation of a C−Cl bond,[11] the $Cr(CO)_3$ tripod plays another role in the alkyl transfer process. Among the possible explanations, we think that the peculiar ability of the chromium entity to form a Sn−Cr metal−metal bond in (arene)tricarbonylchromium complex chemistry would be one of the reasons for our unexpected results. Indeed, it is well-precedented that unstable anionic chromium complexes such as **4** can be trapped with $ClSnPh_3$, leading to the formation of dinuclear complex **5**.[12] The propensity of establishing a Cr−Sn bond can only occur if a partial negative charge is formed due to the *exo* addition of a nucleophile (a hydride, for example, in Scheme 3).

According to literature data, we propose intermediate **6** (Scheme 4), which might highlight the role of the chromium entity. This "pseudo" η^5-cyclohexadienyl intermediate would be formed in the alkyl transfer process

(7) Scott, W. *J. Chem. Soc., Chem. Commun.* **1987**, 1755.

(8) (Fluoroarene)tricarbonylchromium complexes were found to undergo Suzuki reactions using another catalytic system: Widdowson, D. A.; Wilhelm, R. *J. Chem. Soc., Chem. Commun.* **1999**, 2211.

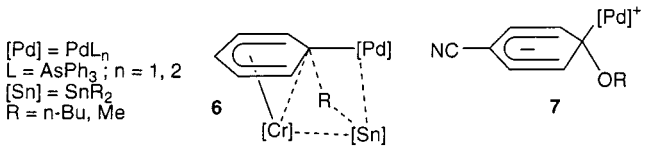
(9) Azizian, H.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *215*, 49.

(10) (a) These results are consistent with those obtained by Wright et al.,[10c] who did not observe a Stille coupling reaction in the case of complexed aryltributylstannane derivatives. In contrast, Johansson et al.[10b] described the formation of coupling products, using phosphines as catalyst ligands. (b) Caldirola, P.; Chowdhury, R.; Johansson, A. M.; Hacksell, U. *Organometallics* **1995**, *14*, 3897. (c) Wright, M. E. *J. Organomet. Chem.* **1989**, *376*, 353.

(11) Kamikawa, K.; Watanabe, T.; Daimon, A.; Uemura, M. *Tetrahedron* **2000**, *56*, 2325.

(12) (a) Djukic, J.-P.; Rose-Munch, F.; Rose, E.; Simon, F.; Dromzee, Y. *Organometallics* **1995**, *14*, 2027. (b) Djukic, J.-P.; Rose-Munch, F.; Rose, E. *J. Am. Chem. Soc.* **1993**, *115*, 6434. (c) Kündig, E. P.; Cunningham, A. F.; Paglia, P.; Simmons, D. P.; Bernardinelli, G. *Helv. Chim. Acta* **1990**, *73*, 386.

Scheme 4



via a partial coordination of the Cr atom to the tin atom, which would weaken the Sn−R bond by increasing its polarity.[13] This might be the driving force of this unexpected alkyl transfer. Moreover, our hypothesis would be consistent with a relevant example of palladium-linked Meisenheimer type species **7** (Scheme 4), which has been recently suggested by Buchwald et al. as one possible intermediate in aryl ether formation.[14] These results raise new mechanistic questions,[15,16] which we continue to address and add further possibilities for the use of arenetricarbonylchromium complexes in addition to their already well-established role in organic synthesis.

In conclusion, reactions of (chloroarene)tricarbonylchromium complexes with hexaalkylditin (or trialkyltin chloride) under palladium catalysis do not proceed by the usual Stille coupling but, instead, give an unprecedented product arising from alkyl migration to the aromatic carbon, yielding the (alkylarene)tricarbonylchromium complex **3**. A plausible mechanism is suggested which involves *a chromium-assisted ipso addition to the aromatic carbon*, shedding light on the crucial role of the $Cr(CO)_3$ tripod, which can interact with the tin moiety. Work is currently in progress to confirm this hypothesis.

Acknowledgment. We thank CNRS and the European Community (TMR program: Grant No. FMRX-CT98-0166) for financial support.

Supporting Information Available: Text giving additional details of the syntheses of compounds reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010004S

(13) Pentacoordinate tin species may form; see for example: Jäkle, F.; Rulkens, R.; Zech, G.; Massey, J. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 4232.

(14) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787.

(15) Other pathways are not excluded. Indeed, one of the reviewers suggested the following plausible mechanism. Because of steric reasons due to the bulky $Cr(CO)_3$ group, the expected stannane product $ArPdSnBu_3$ would not have formed. Instead, the ready dissociation of the arsine would create a vacant binding site on Pd and would allow a competitive α-elimination of Bu_2Sn[16] to give $ArPd(AsPh_3)_2Bu$. Reductive elimination would produce the observed compound. However, our first preliminary results of a NMR study performed with complex **1b**, in perdeuterated THF, showed that, depending on reaction time, doublets appeared at high field that could not be attributed to η^6-arene intermediates but, rather, to labile η^5-cyclohexadienyl complexes.[12b] A complete spectroscopic study is underway and will be reported in due time.

(16) Clark, G. R.; Flower, K. R.; Roper, W. R.; Wright, L. J. *Organometallics* **1993**, *12*, 259.