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Platinum- and palladium-catalysed Kocheshkov redistribution of dialkyltin dichlorides or tetraalkyltins with tin tetrachloride

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The Kocheshkov redistribution reaction of tetraalkyltin or dialkyltin dichlorides with tin tetrachloride is effectively catalysed by platinum(II) or palladium(II) phosphine complexes, yielding alkyltin trichlorides in high yield and with high selectivity.

The activation of Sn–C bonds is an important step in several synthetic organic reactions, *e.g.* Stille-type coupling reactions, transmetallation reactions, nucleophilic allylation reactions, and Kocheshkov redistribution reactions for the synthesis of organotin halides.[1] In comparison with tetraorganotins, Sn–C bond activation of organotin halides is more difficult and follows the order of increasing Sn–C bond dissociation energies ($R_4Sn < R_3SnCl < R_2SnCl_2 < RSnCl_3$).[2]

As part of our interest in metal catalysts for the activation of alkyl–tin bonds and the subsequent use of the resulting metal alkyl species in alkylation reactions, we present here the first results of a study on the use of platinum(II) and palladium(II) phosphine complexes for the Kocheshkov redistribution of tetraalkyl- or dialkyl-tin dichlorides with tin tetrachloride. In particular, the activation of dialkyltin dihalides is notoriously difficult to accomplish and prevents the complete redistribution of tetraalkyltins with tin tetrachloride [eqn. (1)].[3] Known catalysts for this reaction, *e.g.* $POCl_3$, P_2O_5, DMSO, quaternary ammonium salts or SnF_2,[4] require severe conditions and have low selectivity for the desired product. To the best of our knowledge this is the first time that a transition metal-catalysed version of such a redistribution reaction which operates under relatively mild conditions is reported.

$$R_4Sn + 3\ SnCl_4 \rightarrow 4\ RSnCl_3 \qquad (1)$$

Inspired by studies on oxidative addition of Sn–C bonds on Pt(0) complexes[5] and mechanistic work on the Stille-type coupling reaction,[6] we decided to investigate the behaviour of platinum(II) and palladium(II) phosphine complexes in the presence of excesses of dialkyltin dichloride (R_2SnCl_2) and $SnCl_4$ [R = Me, *n*-Bu, *n*-Hex; eqn. (2)].† The results of this approach are shown in Table 1.

$$R_2SnCl_2 + SnCl_4 \rightarrow 2\ RSnCl_3 \qquad (2)$$

The traditional palladium(II) complex for Stille-type coupling reactions[1,6] already resulted in reasonable yields of $BuSnCl_3$ (entry 1). However, premature decomposition of the catalyst into palladium black prevented the reaction from going to completion. Also substantial amounts of $SnCl_2$ were formed as by-product. *cis*-$PtCl_2(PPh_3)_2$ is a more efficient catalyst and almost total consumption of both reactants was observed. Also, *in situ* preparation of the catalyst from $PtCl_2$ and 2 equivalents of PPh_3 was possible, resulting in comparable activity and selectivity (entry 10).

For β-H-containing R groups (R = *n*-Bu, *n*-Hex), a side reaction afforded $SnCl_2$ (up to 21% based on Sn for R = *n*-Hex), the corresponding alkene elimination product, and presumably HCl (not detected). For R = *n*-Bu, lowering of the

Table 1 Results of the redistribution reaction of R_2SnCl_2 with $SnCl_4$ (1:1 molar ratio) in the presence of several Pd and Pt catalysts[a]

Entry	Catalyst	[Catalyst] (mol%)[b]	Solvent[c]	$BuSnCl_3$ (mol%)[d]	$SnCl_2$ (mol%)	Selectivity (%)[e]	Remarks
1	*cis*-$PdCl_2(PPh_3)_2$	1	Neat	35	22	61	Pd-black formation
2	*cis*-$PdCl_2(PPh_3)_2$	0.1	Neat	2.5	1.6	61	Pd-black formation
3	*cis*-$PtCl_2(PPh_3)_2$	1	Neat	72	9	88	
4	*cis*-$PtCl_2(PPh_3)_2$	0.1	Neat	62	16	79	
5	*cis*-$PtCl_2(PPh_3)_2$	0.1	Toluene	84 (80)	13	87	
6	*cis*-$PtCl_2(PPh_3)_2$	0.03	Toluene	83 (80)	14	85	
7	*cis*-$PtCl_2(PPh_3)_2$	0.01	Toluene	78	12	87	
8	*cis*-$PtCl_2(PPh_3)_2$	0.1	Toluene	86	7	92	T = 85 °C, t = 48 h
9	*cis*-$PtCl_2(PPh_3)_2$	0.1	Toluene	83	14	86	T = 130 °C
10	$PtCl_2 + 2\ PPh_3$	0.2	Toluene	81	17	83	
11	*cis*-$PtCl_2(PPh_3)_2$	0.1	*o*-Xylene	70	19	79	
12	*cis*-$PtCl_2(PPh_3)_2$	0.1	*o*-$Cl_2C_6H_4$	85	17	83	
13	*cis*-$PtCl_2(PPh_3)_2$	0.1	*n*-Octane	76	9	89	
14	*cis*-$PtCl_2(PPh_3)_2$ + 5 PPh_3	0.1	Toluene	73	16	82	
15	*cis*-$PtCl_2(PPh_3)_2$ + 10 PPh_3	0.1	Toluene	54	16	77	
16	$PtCl_2$(dppe)	0.1	Toluene	0	0	—	
17	*cis*-$PtCl_2(PPh_3)_2$	0.1	Toluene	87	0	100	R = Me
18	*cis*-$PtCl_2(PPh_3)_2$	0.1	Toluene	67	21	76	R = *n*-Hex

[a] Reaction t = 12 h unless indicated otherwise; R = *n*-Bu unless otherwise stated; T = 110 °C unless otherwise stated. [b] Relative to Bu_2SnCl_2. [c] $[Bu_2SnCl_2]_0 = [SnCl_4]_0$ = 1.0 M when a solvent was used. [d] Yield based on total amount of Sn, determined by ^{119}Sn NMR analysis of the crude reaction mixture with Me_4Sn as external standard. Isolated yield in brackets. [e] Selectivity = $[BuSnCl_3]/([BuSnCl_3]+[SnCl_2]) \times 100\%$.

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catalyst concentration but also working under neat conditions resulted in a decrease of the yield of n-BuSnCl$_3$, but did not affect the selectivity of the reaction. The selectivity is somewhat improved by lowering of the reaction temperature from 110 to 85 °C or by taking n-octane as solvent. However, these variations also lower the overall catalyst activity.

Since eqn. (2) is usually the problematic step for driving eqn. (1) to completion, we decided to test the complete redistribution of n-Bu$_4$Sn with 3 equivalents of SnCl$_4$ in the presence of *cis*-PtCl$_2$(PPh$_3$)$_2$.‡ It was found that this was indeed possible affording n-BuSnCl$_3$ (83% isolated yield) together with only a small amount of SnCl$_2$ (3.7%).

Addition of extra triphenylphoshine to the reaction of n-Bu$_2$SnCl$_2$ with SnCl$_4$ (entries 14, 15) resulted in a decrease of activity and selectivity of the catalyst. The former effect has also been observed for triphenylphosphine–palladium catalysed cross-coupling reactions.[6] Replacement of two monodentate PPh$_3$ ligands by bidentate, 1,2-bis(diphenylphosphino)ethane (dppe), led to complete inactivity of the resulting complex (entry 16) suggesting that dissociation of a phosphine ligand is a crucial mechanistic step in the platinum-catalysed redistribution process.

While the exact mechanism leading to SnCl$_2$ formation remains unknown, the fact that this product is formed for both R = n-Bu and n-Hex but not for R = Me suggests that an intermediate Pt–alkyl species, which has a strong tendency to undergo β-H elimination[7] is involved. In addition, in the reaction of n-Bu$_2$SnCl$_2$ with SnCl$_4$, the presence of the β-H elimination products but-1-ene and but-2-ene could be detected by ^{1}H NMR spectroscopy of the reaction mixture.§ The consumption of reactants in the PtCl$_2$(PPh$_3$)$_2$-catalyzed redistribution reaction of n-Bu$_2$SnCl$_2$ with SnCl$_4$ was monitored by ^{119}Sn NMR (T = 110 °C) and found to be first order in n-Bu$_2$SnCl$_2$ ($k_{\mathrm{obs}} = 1.9 \times 10^{-4}\ \mathrm{s}^{-1}$) and essentially zero order in SnCl$_4$. Since the same rate law was observed for n-BuSnCl$_3$ formation ($k_{\mathrm{obs}} = 1.5 \times 10^{-4}\ \mathrm{s}^{-1}$), it can be concluded that SnCl$_2$ formation ($k_{\mathrm{calc}} = 0.4 \times 10^{-4}\ \mathrm{s}^{-1}$) is a competitive process which takes place after rate determining transmetallation of the (pre)-catalyst. No additional SnCl$_2$ is formed after the reactants have been consumed, which excludes occurrence of a secondary reaction involving decomposition of n-BuSnCl$_3$ (*e.g.* under the influence of spent catalyst) as the source of SnCl$_2$.

A more extensive study on the mechanism of the platinum-catalysed redistribution process and the influence of the nature of the ligands on the catalytic activity and selectivity will be presented in future publications.

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Notes and references

† In a typical experiment, Bu$_2$SnCl$_2$ (252 g, 0.83 mol) was dissolved in toluene (500 mL). Next, SnCl$_4$ (215 g, 0.83 mol) was added to the reaction mixture followed by PtCl$_2$(PPh$_3$)$_2$ (215 mg, 0.27 mmol). The reaction mixture was stirred for 12 h at 110 °C. After cooling to room temperature, the reaction mixture was filtered. After evaporating the solvent *in vacuo*, butyltin trichloride (373 g, 80%) was obtained by a vacuum distillation (90 °C/11 mmHg). The solid SnCl$_2$ (44.5 g, 14%) obtained from filtration, was washed with toluene (3 × 20 mL) and dried in *vacuo* to give an off-white solid. Elemental analysis of SnCl$_2$: Cl, 37.0%; Sn, 61.2%. SnCl$_2$ requires: Cl, 37.4%; Sn, 62.6%.

‡ *Conditions*: 0.033 mol% of *cis*-PtCl$_2$(PPh$_3$)$_2$ (relative to n-Bu$_4$Sn), T = 110 °C, [n-Bu$_4$Sn] = 1.0 M, toluene as solvent. After stirring the reaction mixture for 2 h at 110 °C, the catalyst was added. Stirring was continued for an additional 12 h at this temperature.

§ This experiment was performed analogously to entry 5 (Table 1), but with toluene-d_8 as solvent. The amounts of but-1-ene and but-2-ene (*cis*/*trans*) were found to be 1 and 3%, respectively (relative to the amount of n-Bu$_2$SnCl$_2$): R. K. Harris and B. R. Howes, *J. Mol. Spectrosc.*, 1968, **28**, 191.

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