Journal of Organometallic Chemistry, 345 (1988) 397–403
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Platinum complex catalyzed carbonylative cross-coupling of alkyl iodides with sodium tetraphenylborate; synthesis of alkyl phenyl ketones

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(Received October 1st, 1987)

Abstract

Tetrakis(triphenylphosphine)platinum(0) ($Pt(PPh_3)_4$) is an effective catalyst precursor for the carbonylative cross-coupling of alkyl iodides with sodium tetraphenylborate ($NaBPh_4$) which yields the corresponding alkyl phenyl ketones. In the reaction of n-hexyl iodide with $NaBPh_4$, n-hexyl phenyl ketone was obtained in 60% yield.

Introduction

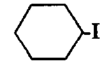
Carbon–carbon bond formation by use of organometallic compounds has been extensively studied [1] and so transition metal complex catalyzed carbonylative cross-coupling of organic halides with organometallic compounds, such as organotin [2], organoaluminum [3], and organoboron [4] compounds, is of current interest. Among the transition metal catalysts, palladium complexes were generally employed in these reactions because of their high transmetallation activity [1–4]. In the palladium-catalyzed reactions, however, organic halides with β-hydrogens on sp^3-carbons could not be effectively carbonylated, since the intermediate σ-alkyl palladium species generated by oxidative addition of the alkyl halides to the metal centres readily undergo β-hydride elimination [5,6]. Therefore, in the palladium-catalyzed reactions, suitable substrates are limited to organic halides such as aryl, vinylic, allylic and benzylic halides, which do not undergo facile β-hydride elimination.

We reported recently, the first example of platinum complex catalyzed carbonylation of organic iodides with β-hydrogens on sp^3-carbons to give the corresponding esters (in alcohols) and aldehydes (under CO-H_2) [7]. Here we report that platinum complexes (especially $Pt(PPh_3)_4$) also catalyze the carbonylative cross-coupling of

0022-328X/88/$03.50

Table 1

Pt-complex catalyzed carbonylative cross-coupling of alkyl halides with $NaBPh_4$ [a]

Run	RX	Pt-complex	Temp. (°C)	Products (%) [b]			
				RCOPh	PhCOPh	Ph-Ph	Ph_3CH
1 [c]	n-$C_6H_{13}I$	$Pt(PPh_3)_4$	100	60(52)	12	8	6
2	n-C_4H_9I	$Pt(PPh_3)_4$	130	45	6	0	47
3		$Pt(PPh_3)_4$	150	40(33)	10	6	40
4	n-$C_6H_{13}Br$	$Pt(PPh_3)_4$	120	0	0	3	1
5	n-$C_6H_{13}Br$	$PtI(Ph)(PPh_3)_2$	120	4	7	9	11
6	n-$C_6H_{13}Br$	$PtCl_2(PPh_3)_2$	120	0	7	15	10
7	n-$C_6H_{13}Cl$	$Pt(PPh_3)_4$	120	0	0	3	1

[a] A mixture of alkyl halide (5 mmol), $NaBPh_4$ (3 mmol), Pt-complex (0.25 mmol) and dioxane (7.5 ml) was stirred for 24 h under 70 kg cm^{-2} of carbon monoxide. [b] Determined by GLC based on the amount of $NaBPh_4$ charged and figures in the parentheses are isolated yields. [c] Under 30 kg cm^{-2} of carbon monoxide.

alkyl iodides with sodium tetraphenylborate ($NaBPh_4$) to give the corresponding alkyl phenyl ketones in good yields (eq. 1).

In the present reaction, a considerable amount of triphenylmethane was always obtained as a by-product. The reaction mechanism and the formation of triphenylmethane are discussed.

Results

Alkyl iodides are effectively carbonylated and coupled with $NaBPh_4$ in the presence of a catalytic amount of $Pt(PPh_3)_4$ to give the corresponding alkyl phenyl ketones in good yields (Runs 1–3 in Table 1). In the reaction of n-hexyl iodide with $NaBPh_4$, n-hexyl phenyl ketone was obtained in 60% yield (Run 1) and secondary alkyl iodides such as cyclohexyl iodide also can be carbonylated by the present catalyst system (Run 3). Alkyl bromides and alkyl chlorides, however, were not consumed at all under the same reaction conditions (Runs 4–7).

Effects of the reaction conditions on the reaction of n-hexyl iodide with $NaBPh_4$ are listed in Table 2. The distribution of the products was very sensitive to both carbon monoxide pressure and reaction temperature. The present reaction did not proceed (Run 8) when the carbon monoxide pressure was below 10 kg cm^{-1}. With pressures of carbon monoxide of 70 kg cm^{-2} above or at higher reaction temperatures ($>$ 120 °C), the selectivity to the alkyl phenyl ketones was reduced (Runs 9–11). Consequently, n-hexyl phenyl ketone was obtained in 60% yield at 100 °C under 30 kg cm^{-2} of carbon monoxide (Run 1).

As can be readily seen from Tables 3 and 4, the product distribution was also dependent on the nature of the catalyst employed. Of the zero-valent transition-metal complexes (Table 3), $Pt(PPh_3)_4$ and $Pt(CO)_2(PPh_3)_2$ showed good catalytic activity

Table 2

Effects of reaction conditions [a]

Run	CO Press. (kg cm^{-2})	Temp. (°C)	Products (%) [b]			
			n-C_6H_{13}COPh	PhCOPh	PhPh	Ph_3CH
8	10	100	8	3	8	3
1	30	100	60	12	8	6
9	70	100	42	9	4	8
10	70	120	38	13	1	45
11	100	120	44	17	1	28

[a] A mixture of n-$C_6H_{13}I$ (5 mmol), $NaBPh_4$ (3 mmol) and $Pt(PPh_3)_4$ (0.25 mmol) was stirred for 24 h. [b] Determined by GLC based on the amount of $NaBPh_4$ charged.

(Runs 10 and 11). With $Pd(PPh_3)_4$, a considerable amount of olefin (1-hexene in the case of n-hexyl iodide) was obtained because of β-hydride elimination and the yield of the corresponding ketone was quite low (Run 14). When $Co_2(CO)_8$ was employed as a catalyst, biphenyl was obtained as the main product (Run 15). For di-valent platinum complexes (Table 4), $PtI(Ph)(PPh_3)_2$ showed a comparable catalytic activity to that of $Pt(PPh_3)_4$ (Run 16). $Pt(n\text{-}Bu)_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ showed some catalytic activity (Runs 17, 18). On the other hand, when $PtCl_2(PPh_3)_2$ combined with $SnCl_2 \cdot H_2O$, which has high catalytic activity for the hydroesterification and hydroformylation of olefins [8,9] and acetylenes [10,11], was used, benzophenone resulting from the carbonylation of $NaBPh_4$, was obtained (Run 19). As for the ligands, triphenylphosphine (cone angle 148° [12a]; pK_a 2.73 [12b]) was the most effective for the present reaction (Runs 10, 11 and 16–18). Other ligands, such as triethylphosphine (Run 12), tri-*o*-tolylphosphine (Run 13), tricyclohexylphosphine (Run 20), triphenylarsine (Run 21), benzonitrile (Run 22), and tri-n-butylphosphite (Run 23) decreased the catalytic activity drastically.

In addition, several organoboron compounds were examined in the present reaction. When other organoborates such as lithium methyltricyclopentylborate and lithium butyltricyclopentylborate were treated with n-hexyl iodide under the same reaction conditions, these borates decomposed and no corresponding ketones were

Table 3

Catalytic activities of several zero-valent metal complexes [a]

Run	Complex	Products (%) [b]			
		n-C_6H_{13}COPh	PhCOPh	PhPh	Ph_3CH
10	$Pt(PPh_3)_4$	38	13	1	45
11	$Pt(CO)_2(PPh_3)_2$	33	16	2	12
12	$Pt(PEt_3)_4$	13	1	3	6
13 [c]	$Pt(dba)_2$	0	1	6	1
14	$Pd(PPh_3)_4$	12	10	3	12
15	$Co_2(CO)_8$	6	4	57	6

[a] A mixture of n-$C_6H_{13}I$ (5 mmol), $NaBPh_4$ (3 mmol) and complex (0.25 mmol) was stirred at 120 °C for 24 h under 70 kg cm^{-2} of carbon monoxide. [b] Determined by GLC based on the amount of $NaBPh_4$ charged. [c] $P(o\text{-}Tol)_3$ (0.4 mmol) was added.

Table 4

Catalytic activities of various di-valent platinum complexes [a]

Run	Pt^{II} complex	Additive	Products (%) [b]			
			$n\text{-}C_6H_{13}COPh$	PhCOPh	PhPh	Ph_3CH
16	$PtI(Ph)(PPh_3)_2$	–	36	10	0	46
17	$Pt(n\text{-}Bu)_2(PPh_3)_2$	–	27	9	1	21
18	$PtCl_2(PPh_3)_2$	–	27	11	5	40
19 [c]	$PtCl_2(PPh_3)_2$	$SnCl_2, 2H_2O$	4	31	1	35
20	$PtCl_2(PCy_3)_2$	–	6	6	6	13
21 [d]	$PtCl_2(PhCN)_2$	$AsPh_3$	2	7	13	2
22	$PtCl_2(PhCN)_2$	–	1	2	20	6
23 [e]	$PtCl_2(PhCN)_2$	$P(O\text{-}n\text{-}Bu)_3$	3	4	5	3

[a] A mixture of $n\text{-}C_6H_{13}I$ (5 mmol), $NaBPh_4$ (3 mmol) and Pt-complex (0.25 mmol) was stirred at 120 °C for 24 h under 70 kg cm^{-2} of carbon monoxide. [b] Determined by GLC based on the amount of $NaBPh_4$ charged. [c] $SnCl_2 \cdot 2H_2O$ (1 mmol) was added. [d] The arsine (0.4 mmol) was added. [e] The phosphite (0.4 mmol) was added.

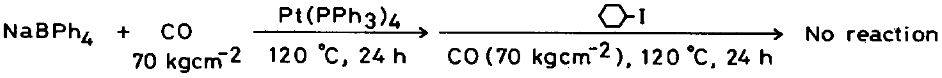
obtained. On the other hand, organoboroles, which could be carbonylated by palladium catalyst via transmetallation [13], were also examined in our reaction. When 1-hexyl and (*E*)-1-octenyl-1,3,2-benzodioxaborole were employed, they were not consumed at all under the reaction conditions studied. In the presence of sodium acetate [13], however nearly 100% of each borole was consumed but the products were intractable mixtures. Furthermore, for the reaction of n-hexyl iodide with triphenylborane (BPh_3) instead of $NaBPh_4$, n-hexyl phenyl ketone was not obtained at all and triphenylmethane was obtained as the sole product (eq. 2). This result was in contrast to that obtained for the palladium complex catalyzed carbonylative cross-coupling of aryl halides with organoboron compounds reported by Kojima et al. [4b].

$$n\text{-}C_6H_{13}\text{-}I \;+\; \underset{70\ kgcm^{-2}}{CO} \;+\; BPh_3 \xrightarrow[120\,^{\circ}C,\ 24\,h]{Pt(PPh_3)_4} \underset{(52)\ \%}{Ph_3CH} \qquad (2)$$

$n\text{-}C_6H_{13}\text{-}I$ was not consumed.

Discussion

There are two possible mechanisms that lead to alkyl phenyl ketones. One is that carbonylation of $NaBPh_4$ takes place first and then its intermediates (such as diboradioxane and boroxine [14]) couple with alkyl iodides to give the products. However, the fact that, when carbonylation of $NaBPh_4$ was carried out in the presence of a catalytic amount of $Pt(PPh_3)_4$ and then treated with cyclohexyl iodide under the same reaction conditions (eq. 3), there was no consumption of cyclohexyl iodide nor formation of cyclohexyl phenyl ketone, precludes this possibility.



(3)

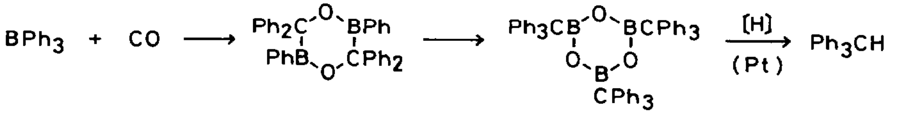
The other route is that an acyl platinum intermediate is generated from the migratory insertion of carbon monoxide into the σ-alkyl platinum bond and subsequently couples with $NaBPh_4$ to give the corresponding ketones. In fact, acyl halides react with various organoborates in the absence of catalysts to give the unsymmetric ketones in high yields [15]. In order to confirm this, the $PtCl(COC_6H_{13}\text{-n})(PPh_3)_2$ complex was treated with $NaBPh_4$ under the same reaction conditions, and n-hexyl phenyl ketone was obtained in 30% yield (eq. 4).

$$\underset{0.1\ \text{mmol}}{\textit{trans}-PtCl(COC_6H_{13}\text{-n})(PPh_3)_2} + \underset{1\ \text{mmol}}{NaBPh_4} \xrightarrow[\text{CO (70 kgcm}^{-2})]{120\,^\circ\text{C, 24 h}} \underset{0.03\ \text{mmol (30 \%)}}{\text{n-}C_6H_{13}COPh} \qquad (4)$$

In this reaction, alkylbenzene which is generated by non-carbonylative cross-coupling (i.e., direct cross-coupling), was not obtained at all. This result suggests that migratory insertion of carbon monoxide into the alkyl platinum bond is much faster than the coupling of phenyl groups in $NaBPh_4$ with alkyl platinum intermediate. Accordingly, transfer of phenyl group of $NaBPh_4$ to platinum intermediate could occur only after the carbonylation of alkyl platinum intermediate to acyl platinum intermediate.

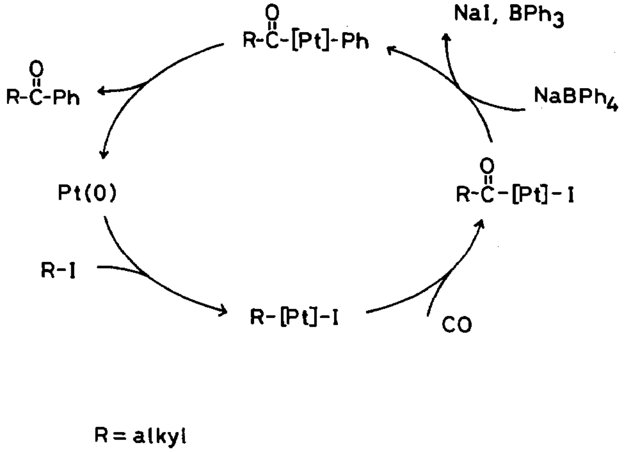
Furthermore, when PhMgBr or PhLi were used instead of $NaBPh_4$ in the present reaction, alkyl phenyl ketone was not obtained at all. This would indicate that direct nucleophilic attack of phenyl anion on acyl moiety in the intermediate acyl platinum complex did not take place and also suggests that the benzoyl platinum intermediate generated from the nucleophilic attack of phenyl anion on coordinative carbon monoxide is not operative in the present catalytic cycle. In other words, transfer of phenyl group to acyl platinum intermediate and subsequent reductive elimination are probably essential in the present reaction (see Scheme 1) and this transmetallation reaction proceeds only from organoborate ($NaBPh_4$), not from other organometallic compounds (PhMgBr and PhLi).

Finally, our reaction always gave triphenylmethane as a by-product. In the reaction of n-hexyl iodide with triphenylborane, triphenylmethane was obtained as a sole product (vide supra; eq. 2). This result indicates that the triphenylmethane was generated from triphenylborane and not from $NaBPh_4$ directly. Hillman found that the carbonylation of trialkylborane actually proceeded smoothly to give diboradioxane and then boroxine [14]. Furthermore, boroxine was converted into trialkyl carbinol in the presence of H_2O_2-NaOH. In our reaction, these intermediates could abstract the hydrogen (probably as hydride) from solvent or others to give triphenylmethane (eq. 5).



(5)

From the results mentioned above, we suggest that this reaction proceeds as outlined in Scheme 1. Oxidative addition of alkyl iodide to an active catalyst centre would afford the σ-alkyl platinum intermediate. Insertion of carbon monoxide and



Scheme 1

the transfer of phenyl group from $NaBPh_4$ to acyl platinum intermediate followed by reductive elimination yields the corresponding alkyl phenyl ketones.

Experimental

Materials

The reagents employed in this study were commercially available and were purified by distillation under argon before use. Lithium methyltricyclopentylborate, lithium butyltricyclopentylborate [15,16] and 1-hexyl [17] and (*E*)-(1)-octenyl-1,3,2-benzodioxaborole [18] were prepared by standard procedures. Carbon monoxide (> 99.9%) was a commercial product and was used without further purification. The transition metal complexes, $Pt(PPh_3)_4$ [19], $Pt(PEt_3)_4$ [20], $Pt(CO)_2(PPh_3)_2$ [21], $Pt(dba)_2$ [22], $Pd(PPh_3)_4$ [23], $PtI(Ph)(PPh_3)_2$ [24], $Pt(n\text{-}Bu)_2(PPh_3)_2$ [25], $PtCl_2(PPh_3)_2$ [26], $PtCl_2(PCy_3)_2$ [27], $PtCl_2(PhCN)_2$ [28] and $PtCl(COC_6H_{13}\text{-}n)(PPh_3)_2$ [29] were prepared by published procedures. $Co_2(CO)_8$ was purchased from Strem Chemicals and used without further purification

General procedure

A mixture of alkyl iodide (5 mmol), $NaBPh_4$ (3 mmol), Pt complex (0.25 mmol; 8.3 mol% based on $NaBPh_4$), and solvent (7.5 ml) was placed in a 50-ml stainless steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirring bar. The unit was sealed and then purged with three pressurization-depressurization cycles of carbon monoxide at 30 kg cm^{-2}. The reactor was then pressurized to 30–70 kg cm^{-2} with carbon monoxide at room temperature, and it was heated to 100–150 ° C during 10 min with stirring and kept at this temperature for 24 h. Rapid cooling terminated the reaction, and the gaseous products were discharged. The resulting orange-brown solution was analyzed by GLC.

Analytical procedure

The products were isolated by vacuum fractional distillation and/or medium pressure column chromatography (absorbent: silica gel or aluminium oxide; eluent:

a mixture of hexane and ethyl acetate). The products were identified by ^{13}C NMR, ^{1}H NMR, IR spectroscopy and elemental analysis. Spectral data (^{1}H NMR, ^{13}C NMR and IR) for all products are consistent with those of authentic samples.

GLC analyses were carried out with Shimadzu GC-4CM and GC-8A chromatographs equipped with 3 mm i.d. × 3 m columns packed with PEG-HT (5% on Uniport HP, 60–80 mesh), Silicone OV-17 (2% on Chromosorb W(AW-DMCS), 80–100 mesh) and Silicone Gum SE-30 (10% on Chromosorb W(AW-DMCS), 60–80 mesh).

^{1}H NMR spectra were recorded at 100 MHz and ^{13}C NMR spectra at 25.05 MHz with a JEOL JNM FX-100 spectrometer, using $CDCl_3$ as a solvent and tetramethylsilane as internal standard. IR spectra were measured on a Nicolet 5MX Fourier transform infrared spectrophotometer. Elemental analysis was carried out at the Microanalytical Center of Kyoto University.

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