The First Example of Carbonylation of Triarylbismuthines: Remarkable Rhodium(I) Catalysis

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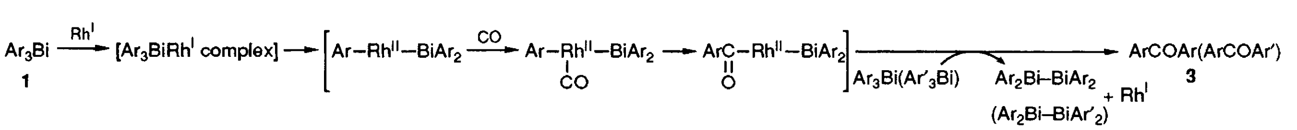
Triarylbismuthines (Ar_3Bi: Ar = C_6H_5, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4) react with atmospheric pressure of carbon monoxide in acetonitrile, tetrahydrofuran or methanol at 25 °C in the presence of a catalytic amount of either $[RhCl(CO)_2]_2$ or $RhCl_3 \cdot 3H_2O$ to produce the corresponding diaryl ketones in good yields, methyl benzoates being also formed in methanol.

The synthetic usefulness of organobismuth compounds has recently increased.[1] However, a clear-cut example of the conversion of a C–Bi bond to a C–C bond seems as yet to be limited to a self-coupling of Ar_3Bi and diaryl ketone formation from Ar_3Bi and aroyl chlorides, both catalysed by palladium(0).[2] We now disclose that a rhodium(I) complex works as a very efficient catalyst for the carbonylation of triarylbismuthines to afford benzophenones and benzoic esters in good yields under very mild conditions.

Treatment of triphenylbismuthine **1a** with atmospheric pressure of carbon monoxide (CO) in tetrahydrofuran (THF) or acetonitrile in the presence of either $RhCl_3 \cdot 3H_2O$ or $[RhCl(CO)_2]_2$ (5 mol%) at 25 °C for 20 h afforded benzophenone **3a** in 46–78% yield (1380–2340% yield based on rhodium salt) together with a trace amount of biphenyl **4a**, while in methanol methyl benzoate **2a** was produced as well as **3a**. The yield of **3a** was not improved by a longer reaction time. The reaction proceeded even by the use of 1 mol% of $[RhCl(CO)_2]_2$, the yield of **3a** in acetonitrile being 29% and the turnover number being increased to 44 from the 23 of 5 mol% use. With other easily available triarylbismuthines such as **1b**, **1c** and **1d** the corresponding esters **2** and diaryl ketones **3** were also formed in good yields. Typical results are shown in Table 1. Other rhodium compounds such as $Rh_2(OAc)_4$, $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$ were only slightly effective, and thus, a low yield (12–17%) of **3a** was obtained in THF under similar conditions. Metal salts such as $RuCl_3$, $IrCl_3$ and $PdCl_2$ were almost ineffective.



Scheme 1

Table 1 Carbonylation of triarylbismuthines with CO in the presence of a rhodium(I) complex

Bismuth compound (1 mmol)	Rh-complex[a] (mmol)	Solvent (10 ml)	Products and yield (%)[b]		
			2	**3**	**4**
1a	$RhCl_3 \cdot 3H_2O$	MeCN	0	49	Trace
1a	$RhCl_3 \cdot 3H_2O$	THF	0	46	1
1a	$RhCl_3 \cdot 3H_2O$	MeOH	17	58	0
1a	$[RhCl(CO)_2]_2$	MeCN	0	78	Trace
1a	$[RhCl(CO)_2]_2$[c]	MeCN	0	29	1
1a	$[RhCl(CO)_2]_2$	MeOH	15	65	0
1a	$[RhCl(CO)_2]_2$[c]	MeOH	3	24	0
1b	$RhCl_3 \cdot 3H_2O$	MeOH	10	51	17
1b	$[RhCl(CO)_2]_2$	MeCN	0	72	9
1b	$[RhCl(CO)_2]_2$	THF	0	51	10
1c	$RhCl_3 \cdot 3H_2O$	MeOH	26	29	2
1c	$[RhCl(CO_2)]_2$	MeCN	0	75	1
1d	$[RhCl(CO_2)]_2$	MeCN	0	67(64)[d]	1

[a] 0.05 mmol of rhodium(I) complex used except where otherwise stated. [b] Determined by GLC: based on triarylbismuthine, 3 mmol of **2** and 1.5 mmol of **3** and **4** correspond to 100% yield, respectively. [c] 0.01 mmol rhodium(I) complex used. [d] Isolated yield.

$$\underset{\mathbf{1}}{Ar_3Bi} \xrightarrow[\text{Solvent, 25 }^{\circ}\text{C, 20 h}]{\text{Rh-complex–CO(1 atm)}} \underset{\mathbf{2}}{ArCO_2Me} + \underset{\mathbf{3}}{ArCOAr} + \underset{\mathbf{4}}{ArAr}$$

(**a**: Ar = Ph, **b**: Ar = 4-MeC_6H_4, **c**: Ar = 4-$MeOC_6H_4$, **d**: Ar = 4-ClC_6H_4)

Although the exact nature of the reaction is still obscure, the most plausible pathway seems to be the initial coordination of **1** to rhodium(I) followed by aryl migration from bismuth to rhodium to produce an organorhodium compound and by CO insertion to the produced C–Rh bond (Scheme 1). Rhodium(III) chloride may be reduced to some rhodium(I) species under the reaction conditions. The separately confirmed retardation of the $RhCl_3 \cdot 3H_2O$-catalysed carbonylation by addition of triphenylphosphine (*e.g.* the yield of **3a** decreased from 46 to 4% by addition of 2 mmol of Ph_3P in THF) is explicable in terms of preferred coordination of the stronger base Ph_3P to Rh^I than Ar_3Bi. The aryl migration process may also be considered as oxidative addition of a C–Bi bond to Rh^I, the precedent of which is found in the proposal of addition of a C–Hg bond to Rh^I in the Rh^I-mediated carbonylation of some vinyl- and aryl-mercury(II) chlorides.[3] When equimolar amounts of triphenylbismuthine **1a** (0.50 mmol) and tri-*p*-tolylbismuthine **1b** (0.50 mmol) were treated with CO(1 atm) in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ (0.05 mmol) in acetonitrile at 25 °C for 20 h, a mixture of **3a** (0.26 mmol), **3b** (0.24 mmol) and unsymmetrical 4-tolyl phenyl ketone (0.38 mmol) was obtained together with minor amounts of biaryls. The formation of three different ketones in this competitive reaction clearly shows the occurrence of the intermolecular reaction between an intermediate aroylrhodium(II) compound and the starting triarylbismuthines.† Other compounds of group 15 elements such as triphenylantimony and triphenylarsine were not activated at all in this Rh^I-catalysed system.

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References

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† In the scheme we proposed the formation of $Ar_2Bi–BiAr_2$. Our preliminary experiment showed that $Ph_2BiBiPh_2$, prepared from Ph_2BiCl by the reported method,[4] also reacted with CO in the presence of $[RhCl(CO)_2]_2$ catalyst to afford **3a** in *ca.* 30% yield based on the dibismuthine. The fate of bismuth in our present carbonylation may be metallic bismuth, though not yet clear, since, for example, the formation of 78% (1.17 mmol) yield of **3a** from 1 mmol of **1a** (Table 1) means the transfer of 2.34 out of 3 phenyl groups to the product.