

Novel Palladium-Catalyzed Carbonylation of Organic Halides by Chloroform and Alkali

Vladimir V. Grushin and Howard Alper*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

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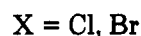
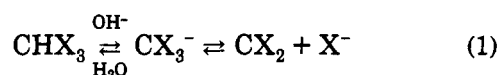
Aromatic, vinylic, and benzylic halides were catalytically carbonylated by CO generated *in situ* from chloroform and aqueous alkali, in the presence of tertiary phosphine-palladium complexes (1-5 mol %). The carbonylation occurred at ambient temperature under N₂, affording the corresponding carboxylic acids in up to 92% isolated yield. Under the same conditions, benzal bromide underwent catalytic reductive coupling to a 1:4 mixture of *cis*- and *trans*-stilbenes. A labeling experiment with ¹³CHCl₃ showed that the source of the C₁ unit in the carbonylation is chloroform. Triphenylphosphine complexes of ruthenium, rhodium, and palladium were found to catalyze the alkaline hydrolysis of chloroform to carbon monoxide. A carbonyl complex, [(Ph₃P)₂Rh(CO)Cl], was synthesized by treatment of Wilkinson's catalyst with chloroform in the presence of KOH.

Introduction

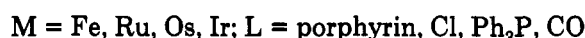
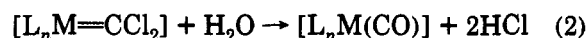
The transition-metal-catalyzed carbonylation of various organic substrates is of significant importance in organic synthesis. A wide variety of valuable organic products have become readily available due to the development of inexpensive, simple, and highly efficient methods for the carbonylation of organic halides, olefins, alkynes, dienes, alcohols, and even aromatic and saturated hydrocarbons.¹ The indispensable participant of the carbonylation processes is CO, by definition. Carbon monoxide is cheap, reactive, and readily available on an industrial scale. At the same time, it possesses a number of disadvantages. First of all, CO is a highly toxic gas which must be stored and transported in stainless-steel tanks and cylinders. When carbon monoxide is bubbled through a reaction mixture, besides losses (which can be substantial sometimes), there is always a risk of clogging the gas inlet tubes. In this event, the catalytic process is often terminated with possible leakage of the toxic gas, or even an explosion. Therefore, the development of a new and safe technique where carbon monoxide is not introduced to the reaction mixture, but gradually generated *in situ* and simultaneously consumed in the course of the process, is a highly desirable goal. Obviously, the carbon monoxide precursor should be a relatively nontoxic solid or liquid material which is readily available, inexpensive, and easy to handle. Carbonylation has been realized by the use of reactants containing a carbonyl group such as methyl formate.² However, there are no examples of the carbonylation of organic substrates in the absence of either carbon monoxide or a carbonyl transfer agent. We now report the first examples of the novel Pd-catalyzed carbonylation of organic compounds by chloroform in the presence of alkali.

Like CO, dihalocarbenes (CCl₂ and CBr₂) are carbon(II) compounds. Theoretically, alkaline hydrolysis of CX₂ (X = Cl, Br) should lead to carbon monoxide. However, both carbenes are quite unreactive toward water and even

concentrated alkali. In fact, they can be efficiently generated from the corresponding haloform and 50% NaOH under biphasic or phase-transfer-catalysis (PTC) conditions at room temperature (eq 1).^{3,4}



Unlike free dihalocarbenes, some of their complexes with transition metals are stable enough to be isolated and fully characterized by physical methods, including single-crystal X-ray diffraction. The brilliant work by Mansuy,^{5,6} Roper,⁷⁻¹⁰ and co-workers has demonstrated unambiguously the existence and stability of such dichlorocarbene complexes and reliably established their structures. It has been shown that, in contrast to noncoordinated dichlorocarbene, the carbon-chlorine bonds in coordinated dichlorocarbene ligands are highly reactive toward nucleophiles.⁵⁻¹⁰ For instance, in the presence of water, the dichlorocarbene complexes undergo smooth and irreversible hydrolysis at ambient temperature, to give the corresponding *carbonyl* compounds in high yield (eq 2).⁷⁻¹⁰



It seemed conceivable to us that dichlorocarbene, generated from chloroform and alkali under biphasic or

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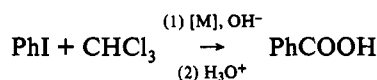
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Table I. Transition-Metal-Catalyzed Carbonylation of Iodobenzene (1.5 mmol) with Chloroform under Biphasic Conditions



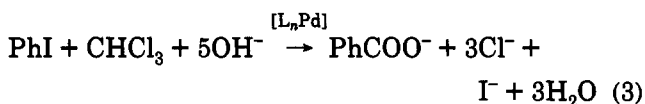
entry no.	[M] (amt, mmol)	concn of KOH, % ^a	vol of CHCl ₃ , mL	reacn temp, °C	reacn time, h	isolated yield, % ^b
1	[(Ph ₃ P) ₂ Pd(I)Ph] (0.075)	60	1	22	24	52
2	[(Ph ₃ P) ₂ PdCl ₂] (0.075)	60	1	22	24	72
3	[(Ph ₃ P) ₂ PdCl ₂] (0.075)	50	4	60	20	49
4	[(Ph ₃ P) ₂ PdCl ₂] (0.075) + Ph ₃ P (0.30)	50	4	60	24	12
5 ^c	[(Ph ₃ P) ₂ PdCl ₂] (0.15)	60	1.5	22	24	69
6	[(dppe)PdCl ₂] (0.075) ^d + dppe (0.15)	50	4	22	96	59
7	[(dppe)PdCl ₂] (0.075) ^d	60	1	22	24	65
8	[(dppe)PdCl ₂] (0.075) ^d	40	1	22	24	64
9	[(dppe)PdCl ₂] (0.075) ^d	20	1	22	24	46
10	[(Ph ₃ P) ₂ Pd ₂ Ph ₂ (μ-OH) ₂] (0.037)	60	1	22	24	57
11	[(Ph ₃ P) ₂ Pd ₂ Ph ₂ (μ-OH) ₂] (0.037)	60	2	22	24	42
12	[(Ph ₃ P) ₂ Pd ₂ Ph ₂ (μ-OH) ₂] (0.037)	50	4	22	24	44
13	[(Ph ₃ P) ₂ Pd ₂ Ph ₂ (μ-OH) ₂] (0.037)	50	4	60	24	51
14	[(Ph ₃ P) ₃ RhCl] (0.075)	50	4	60	23	20
15	[(Ph ₃ P) ₂ NiCl(1-C ₁₀ H ₇)] (0.075) + Ph ₃ P (0.15)	40	3	22	24	0
16	[(Ph ₃ P) ₃ RuCl ₂] (0.075)	50	3	22	65	0

^a 5–6 g of aqueous alkali. ^b After purification by vacuum sublimation. ^c 3.0 mmol of PhI. ^d dppe = 1,2-bis(diphenylphosphino)ethane.

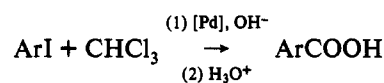
PTC conditions in the presence of an appropriate transition-metal compound, could be used for the *in situ* preparation of the corresponding carbonyl complexes. The latter then could be utilized for the catalytic carbonylation of an organic substrate, with the catalytic cycle maintained at the expense of the continuous generation of CCl₂.

Results and Discussion

Aromatic and Vinylic Halides. We have found that iodobenzene can be successfully carbonylated with chloroform in the presence of catalytic amounts of phosphine-palladium complexes under biphasic conditions (eq 3).



The reaction (eq 3) proceeds at room temperature under a nitrogen atmosphere. Table I summarizes the catalytic synthesis of benzoic acid from iodobenzene and chloroform in the presence of transition-metal complexes under various conditions. As can be seen, the palladium complexes are better catalysts than Wilkinson's complex, [(Ph₃P)₃RhCl], whereas the complexes of nickel and ruthenium exhibited no catalytic activity. No conversion of iodobenzene was observed in the absence of transition-metal compounds under the same conditions. High concentrations of aqueous KOH (40–60%) worked well for the reaction; however, when the alkali concentration was decreased to 20%, the yield of benzoic acid was significantly lower (e.g., entries 7–9). Chloroform can be used as both the reagent and the organic phase. An approximately 8:1 molar ratio of chloroform to iodobenzene appeared to be optimal for the reaction, providing it with enough CO precursor and creating an organic phase of sufficient volume for an efficient biphasic process. Dilution of the organic phase with benzene slowed down the reaction. A substantial retardation of the process was also observed when extra triphenylphosphine was added to the reaction catalyzed by [(Ph₃P)₂PdCl₂] (entries 3 and 4).

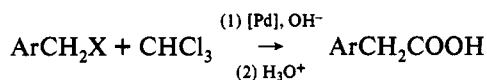
Table II. Biphasic Carbonylation of Iodoarenes with Chloroform, Catalyzed by [(Ph₃P)₂PdCl₂]^a

entry no.	Ar	isolated yield, % ^b	entry no.	Ar	isolated yield, % ^b
1	C ₆ H ₅	54–72	6	3-CH ₃ OC ₆ H ₄	91–92
2	4-CH ₃ C ₆ H ₄	54–76	7	4-ClC ₆ H ₄	54–65
3	3-CH ₃ C ₆ H ₄	77–81	8	3-ClC ₆ H ₄	76–89
4	2-CH ₃ C ₆ H ₄	43–45	9	1-C ₁₀ H ₇	78–81
5	4-CH ₃ OC ₆ H ₄	60–73			

^a Reaction conditions: 1.5 mmol of iodoarene, 5 g of 60% KOH, 1 mL of CHCl₃, 0.075 mmol of [(Ph₃P)₂PdCl₂], N₂, 22 °C, 24 h. ^b After purification by vacuum sublimation.

The reaction is simple and clean, leading to benzoic acid, which was isolated from the aqueous layer in the usual manner and purified by vacuum sublimation. Surprisingly, benzoylformic acid (the double-carbonylation product) was found by GC-MS in the *organic* layer of the reaction mixtures. Since the existence of the acid in an organic phase of low polarity in the presence of aqueous alkali is unlikely, it must have resulted from decomposition of some relatively stable, nonacidic complex or precursor in the course of the GC analysis. In a number of cases, besides benzoylformic acid (ca. 1–5%) and unreacted iodobenzene, trace amounts of dichloriodomethane, hexachloroethane, and biphenyl were found by GC-MS in the reaction mixtures.

Several iodoarenes containing various substituents at the ortho, meta, and para positions of the ring were successfully carbonylated with chloroform under biphasic conditions (Table II). Each iodoarene was reproducibly carbonylated at least twice. As anticipated, the yield of *o*-toluic acid was lower than that of the meta and para isomers. Interestingly, meta-substituted substrates gave slightly better yields than their para isomers. This cannot be rationalized in terms of steric factors since, unlike ortho-substituted benzenes, meta and para isomers possess almost the same effective steric bulk. Under the same

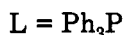
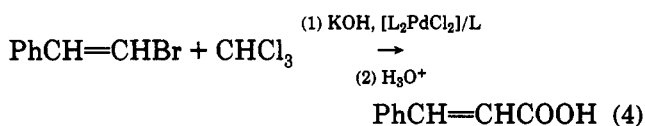
Table III. Biphase Carbonylation of Benzylic Halides with Chloroform, Catalyzed by [(Ph₃P)₂PdCl₂]^a

entry no.	substrate	additive (amt, equiv)	isolated yield, % ^b
1	C ₆ H ₅ CH ₂ Br		60–70
2	C ₆ H ₅ CH ₂ Cl		<0.5
3	C ₆ H ₅ CH ₂ Cl	KBr (1)	1
4	C ₆ H ₅ CH ₂ Cl	CeCl ₃ ·6H ₂ O (0.01)	10
5	C ₆ H ₅ CH ₂ Cl	CeCl ₃ ·6H ₂ O (0.1)	11.5
6	4-CH ₃ C ₆ H ₄ CH ₂ Br		59–68
7	3-CH ₃ C ₆ H ₄ CH ₂ Br		54–60
8	2-CH ₃ C ₆ H ₄ CH ₂ Br		43–47
9	2-C ₁₀ H ₇ CH ₂ Br		42–49
10	4-F-C ₆ H ₄ CH ₂ Br		26–45

^a Reaction conditions: 1.5 mmol of benzylic halide, 4 g of 50% KOH, 1.2 mL of CHCl₃, 0.015 mmol of [(Ph₃P)₂PdCl₂], N₂, 22 °C, 24 h. ^b After purification by vacuum sublimation.

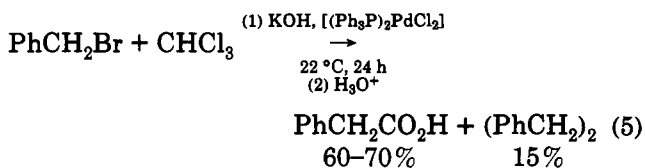
conditions, bromobenzene exhibited much lower reactivity than the aryl iodides, to give benzoic acid in only trace amounts.

It is remarkable that, unlike the dihalopropanation of olefins,^{3,4} carbonylation with chloroform/alkali readily proceeds in the absence of any phase-transfer catalyst. This makes possible the carbonylation not only of haloarenes but also of vinylic halides. For instance, *trans*-cinnamic acid was isolated in 50% yield from the palladium-catalyzed reaction between β -bromostyrene and CHCl₃/KOH (eq 4). The reaction (eq 4) gave much poorer



yield (17%) when it was conducted without extra triphenylphosphine. Probably, the lower reactivity of the carbon–bromine bond toward zerovalent palladium species requires better stabilization of the latter by an excess triphenylphosphine ligand.

Benzylic Halides. Under similar conditions, benzyl bromide reacts with chloroform and aqueous KOH in the presence of catalytic amounts of [(Ph₃P)₂PdCl₂] (1 mol %) to give phenylacetic acid (eq 5; Table III). The reaction also produces noticeable amounts of bibenzyl (ca. 15%), which was isolated from the organic phase of the two-phase system.

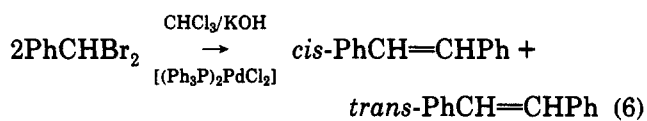


Benzyl chloride exhibited much lower reactivity toward carbonylation with chloroform. Only traces of phenylacetic acid (<1%) were formed in the reaction of benzyl chloride with CHCl₃ under the same conditions. In an attempt to enhance the reactivity of benzyl chloride, the carbonylation was conducted in the presence of potassium bromide or hydrated cerium chloride. Since nucleophilic

substitution of Cl⁻ for Br⁻ at a benzylic carbon atom should be quite facile (although reversible), one could anticipate better yields of phenylacetic acid from the reaction of benzyl chloride with chloroform in the presence of bromide anion. Nonetheless, the yield of PhCH₂COOH remained negligible when the carbonylation of benzyl chloride was conducted with excess KBr (Table III, entry 3). The beneficial effect of hydrated cerium chloride on the nickel cyanide catalyzed and phase-transfer-catalyzed carbonylation of benzylic chlorides has been recently discovered.¹¹ Indeed, addition of CeCl₃·6H₂O (1 or 10 equiv with respect to the palladium catalyst) increased the yield quite noticeably; however, the obtained yields (10 and 11.5%, respectively; see entries 4 and 5) were still too low to be considered even modest.

A number of benzylic bromides with various substituents on the benzene ring were carbonylated with chloroform in the presence of [(Ph₃P)₂PdCl₂] (entries 6–10), to give the corresponding arylacetic acids in moderate to good yields. It is noteworthy that the reaction of *p*-nitrobenzyl bromide did not furnish any acid but resulted, instead, in a complicated mixture of products which we failed to identify.

When α,α -dibromotoluene (benzal bromide) was reacted with chloroform and alkali under the same conditions, no carbonylation occurred. Instead of carboxylic acids, a mixture of *cis*- and *trans*-stilbene (1:4) was isolated in 61% yield from the organic layer (eq 6).



Reaction 6 represents an interesting example of *catalytic* reductive homocoupling of *gem*-dihalides. In most cases, this process requires *stoichiometric* amounts of various low-valent metal reagents.^{12,13a} Recently, a semicatalytic conversion of benzal halides to stilbenes in the presence of [Fe(CO)₅] (25 mol %) was described.¹³ In a catalytic manner, the reductive dimerization of dihalides can be performed at 130 °C, with organodisilanes as reducing agents and [(Ph₃P)₄Pd] as the catalyst.¹⁴ Although our catalytic reaction (eq 6) gives slightly lower (but still satisfactory) yield, it readily occurs at ambient temperature and employs inexpensive chloroform instead of organosilicon reductants. Evidently, the divalent carbon species which are generated under the reaction conditions from CHCl₃ are responsible for the reduction. No reductive homocoupling of benzal bromide was observed when chloroform was replaced by benzene in the reaction.

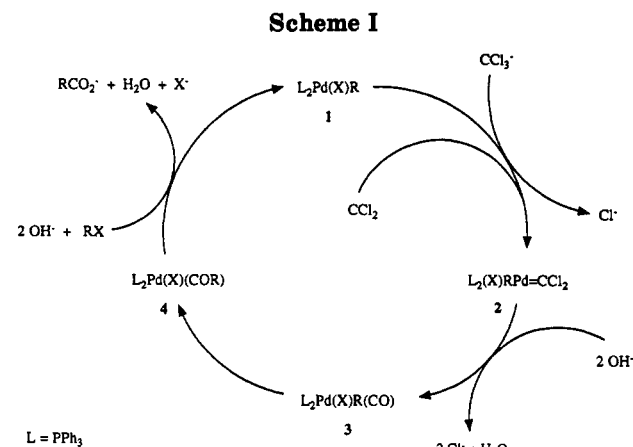
Mechanistic Studies and Considerations. The carboxy group (eqs 3–5) originates from chloroform and no other source, e.g. carbonates which often contaminate alkali, due to the reaction with CO₂ from the air. This was proved by running the reaction of iodobenzene with ¹³CHCl₃ (99% isotopic purity), in the presence of [(Ph₃P)₂PdCl₂]. Both the ¹³C NMR and mass-spectral studies showed that the benzoic acid isolated from the

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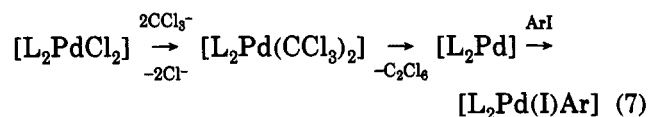
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reaction mixture was Ph¹³COOH of high chemical and isotopic purity (>98%). It is unlikely that the palladium-catalyzed biphasic reaction of iodoarenes with chloroform involves cross-coupling to give α,α,α -trichlorotoluene, followed by its alkaline hydrolysis. No benzoic acid was obtained when PhCCl₃ was reacted with chloroform and alkali under the standard reaction conditions, with or without [(Ph₃P)₂PdCl₂]. Indeed, alkaline hydrolysis of α,α,α -trichlorotoluene under biphasic or even PTC conditions occurs at elevated (80 °C) temperature.¹⁵

A possible mechanism for the palladium-catalyzed biphasic carbonylation of iodoarenes with chloroform is shown in Scheme I. If the added Pd(II) complex does not contain a σ -organic ligand, it is first reduced to a Pd(0) species, which then oxidatively adds the organic halide to give 1 or its analogue. The Pd(II) to Pd(0) reduction could take place at the expense of the coordinated phosphine ligand in the presence of alkali.¹⁶ Another possibility is substitution of the chloro ligands in [(Ph₃P)₂PdCl₂] by two trichloromethyl anions, followed by reductive elimination of hexachloroethane (eq 7). The latter was indeed found among the reaction products (see above).



In principle, several pathways could lead to the palladium dichlorocarbene complex 2 under the reaction conditions. A direct addition of the interface-generated CCl₂ to the (σ -organyl)palladium complex 1 might take place. Another path involves coordination of the trichloromethyl anion with the palladium center, followed by the loss of one chloride anion. The latter may migrate to the metal prior to elimination from the complex. Such isomerization of trichloromethyl complexes likely takes place in the synthesis of dichlorocarbene complexes from (CCl₃)₂Hg and the corresponding transition-metal compounds.^{7-10,17} The formation of CHCl₂I in the reaction (see above) is in good agreement with this mechanistic model. Obviously, a transition-metal complex containing both dichlorocarbene and iodo ligands can isomerize to a

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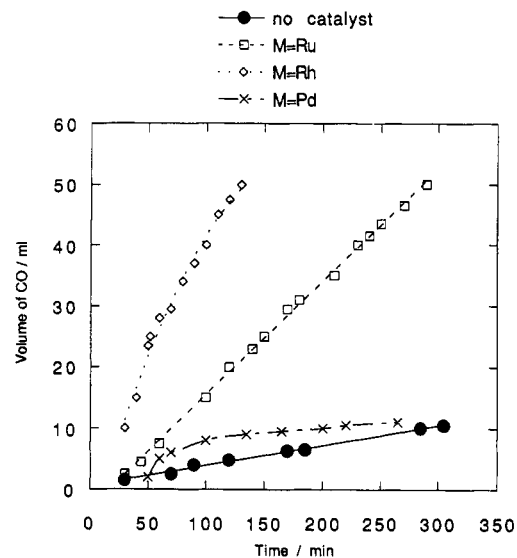


Figure 1. Transition-metal-catalyzed alkaline hydrolysis of chloroform to CO. (KOH (3g), H₂O (3 mL), CHCl₃ (3 mL), [M] (0.1 mmol), 21 °C; [M] = [(PPh₃)₃RuCl₂], [(PPh₃)₃RhCl], [(PPh₃)₂PdCl₂]).

σ -dichloriodomethyl complex. Elimination of CCl₂I⁻, followed by protonation, would result in CHCl₂I.¹⁸

The dichlorocarbene complexes easily hydrolyze in the presence of aqueous alkali. The resulting carbonyl complex 3 transforms to the acyl (aroyl) species 4, which then reacts in the usual manner,¹ as anticipated had it been formed from CO. Poisoning of the palladium catalyst could, in addition to the common ways, take place as a result of the intramolecular electrophilic attack of the dichlorocarbene ligand at the phenyl ring of the triphenylphosphine ligand¹⁹ or due to the reaction between free CCl₂ and PPh₃.²⁰

It is noteworthy that triphenylphosphine complexes of ruthenium, rhodium, and palladium indeed catalyze the alkaline hydrolysis of chloroform to CO. While very sluggish in the absence of transition-metal complexes,^{4,20} the hydrolysis of chloroform was significantly accelerated by [(Ph₃P)₃RuCl₂] and [(Ph₃P)₃RhCl] (Figure 1). The reactions were monitored by measuring the volume of evolving CO with a mercury gas buret. Despite the fact that precise kinetic measurements are inapplicable to biphasic systems containing concentrated alkali,²¹ Figure 1 reflects the general qualitative pattern quite clearly. Wilkinson's catalyst induced the hydrolysis more efficiently than the ruthenium complex [(Ph₃P)₃RuCl₂]. No evidence for catalyst deactivation was observed in both cases after more than 20 catalytic turnovers. In contrast, the palladium complex [(Ph₃P)₂PdCl₂] was far less durable as the hydrolysis catalyst. Under the same conditions, precipitation of palladium metal and complete loss of the catalytic activity were observed ca. 1–1.5 h after the hydrolysis began (see the characteristic shape of the corresponding curve in Figure 1). The lack of metal deposition during the palladium-catalyzed carbonylation

(18) Another pathway for the formation of dichloriodomethane includes addition of iodide anion to dichlorocarbene, followed by protonation of CCl₂I⁻.⁴

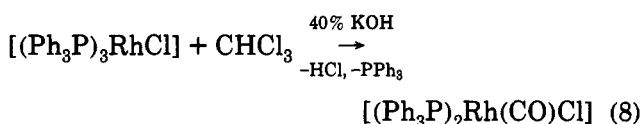
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of iodoarenes with chloroform is obviously due to the facile oxidative addition of the carbon-iodine bond to the zerovalent palladium species formed in the course of the reaction. As clearly seen from Figure 1, the transition-metal-catalyzed hydrolysis of chloroform has an induction period. The latter is probably due to a conversion of the original complexes to the catalytically active species. Obviously, some proportion of the carbonylation products could arise from CO which is slowly generated *in situ* by the hydrolysis of dichlorocarbene.

Most palladium carbonyl compounds, as well as acyl (aroyl) complexes in the presence of alkali, are too unstable for isolation and characterization. However, the rhodium carbonyl complex $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}]$ was isolated from the reaction between Wilkinson's catalyst and chloroform in the presence of alkali (eq 8). Spectral characteristics (IR, ^{31}P NMR) of the isolated carbonyl-rhodium complex were identical with those of an authentic sample prepared from $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ and CO.²²



In conclusion, a novel methodology has been developed for the transition-metal-catalyzed carbonylation of organic substrates with chloroform in the presence of alkali, instead of CO gas. It has been unambiguously demonstrated that carbonyl complexes of transition metals can be obtained from their non-carbonyl precursors and dichlorocarbene generated *in situ* from CHCl_3 and aqueous alkali.

Experimental Section

Spectral measurements were carried out using the following equipment: Varian XL 300 (^1H , ^{13}C , and ^{31}P NMR), Bomen MB-100 (FT-IR), and VG 5050 Micromass (mass spectra). Melting point determinations were made on a Fisher-Johns apparatus. Organic halides, tertiary phosphines, $^{13}\text{CHCl}_3$, and other chemicals were purchased from Aldrich, Strem, Organometallics, and MSD Isotopes chemical companies. Chloroform (stabilized with 0.5% EtOH) was used as received. The complexes $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$,²³ $[(\text{dppe})_2\text{PdCl}_2]$,²⁴ $[(\text{Ph}_3\text{P})_2\text{Pd}_2\text{Ph}_2(\mu\text{-OH})_2]$,¹⁶ $[(\text{Ph}_3\text{P})_3\text{-RhCl}]$,²² $[(\text{Ph}_3\text{P})_3\text{RuCl}_2]$,²⁵ and $[(\text{Ph}_3\text{P})_2\text{Ni}(1\text{-C}_{10}\text{H}_7)\text{Cl}]$ ²⁶ were prepared as described in the literature.

Preparation of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{I})\text{Ph}]$. A mixture of $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (1.01 g; 1.44 mmol), Ph_3P (1.55 g; 5.9 mmol), 40% NaOH (5 g), and benzene (8 mL) was stirred under N_2 , first at room temperature (22 h) and then at 65 °C (7 h). Degassed benzene (22 mL) was added to the warm mixture upon stirring. The clear, yellow organic layer containing Pd(0) phosphine complexes^{16,27} was separated warm, immediately treated with PhI (0.40 g; 1.96 mmol), and kept at room temperature under N_2 overnight. The reaction mixture was worked up in air. The solution was filtered and evaporated, and the residual oil was treated with ethanol. Precipitated crystals were washed with ethanol and dried under vacuum. The yield of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{I})\text{Ph}]$ (identical with an authentic sample) was 1.13 g (94%).

General Procedure for the Carbonylation of Iodoarenes with $\text{CHCl}_3/\text{Alkali}$. To a degassed (freeze-pump-thaw) mixture of aqueous KOH, chloroform, and iodoarene in a 150-mL Schlenk tube was added $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (see Table II for specifics), and the mixture was vigorously stirred at 22 °C under N_2 for 24 h. Water (30 mL) and ether (20 mL) were added; the aqueous layer was separated, acidified with 20% HCl, and extracted with ether (3 × 30 mL). The combined ether solutions were dried over MgSO_4 , filtered, and evaporated to give the crude acid, which was purified by vacuum sublimation. The acids were found to be pure and identical (melting point, ^1H NMR spectroscopy, mass spectrometry) with authentic samples.

Preparation of Cinnamic Acid from β -Bromostyrene. A mixture of β -bromostyrene (0.270 g; 1.47 mmol), CHCl_3 (1 mL), KOH (2 g), water (2 mL), $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (0.052 g; 0.074 mmol), and PPh_3 (0.058 g; 0.221 mmol) was vigorously stirred at 22 °C under N_2 for 24 h. Workup of the reaction mixture as described above resulted in 0.110 g (50%) of spectroscopically (^1H NMR) pure *trans*-cinnamic acid.

General Procedure for the Carbonylation of Benzylic Bromides with $\text{CHCl}_3/\text{Alkali}$. An oxygen-free mixture of benzylic bromide (1.56 mmol), 50% KOH (4 g), CHCl_3 (1.5 mL), and $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (11 mg; 0.0157 mmol) was stirred at 22 °C under N_2 for 24 h (Table III). Isolation of the acids and their purification were conducted as described above.

Reductive Homocoupling of Benzal Bromide. An oxygen-free mixture of 50% KOH (4 g), CHCl_3 (1.5 mL), PhCHBr_2 (0.399 g; 1.6 mmol), and $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (11.5 mg; 0.016 mmol) was stirred at 22 °C under N_2 for 24 h. The mixture was extracted with ether, the combined ether extracts were evaporated, and column chromatography of the residue gave 88 mg (61%) of a 1:4 mixture of *cis*- and *trans*-stilbenes (^1H NMR, GC-MS).

Carbonylation of Iodobenzene with $^{13}\text{CHCl}_3/\text{Alkali}$. A mixture of KOH (3 g), H_2O (2 mL), PhI (0.30 g; 1.47 mmol), benzene (0.5 mL), $^{13}\text{CHCl}_3$ (0.5 g; 4.15 mmol), and $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (110 mg; 0.15 mmol) was vigorously stirred at 22 °C under nitrogen for 72 h. The acid ($\text{Ph}^{13}\text{COOH}$) was isolated and purified in the usual manner. The yield was 83 mg (46%); mp 122–123 °C. ^{13}C NMR (CDCl_3): δ 172.6 ppm. MS (*m/e*, 70 eV): 123 (78) M^+ , 106 (100) $\text{M}^+ - \text{OH}$, 77 (80) $\text{M}^+ - ^{13}\text{COOH}$.

Transition-Metal-Catalyzed Alkaline Hydrolysis of Chloroform. A transition-metal complex (0.10 mmol of $[\text{L}_3\text{RuCl}_2]$, $[\text{L}_3\text{RhCl}]$, or $[\text{L}_2\text{PdCl}_2]$; $\text{L} = \text{PPh}_3$) was added under nitrogen to an oxygen-free mixture of KOH (3 g), H_2O (3 mL), and CHCl_3 (3 mL) placed in a 100-mL Schlenk tube equipped with a magnetic stirrer, magnetic stirring bar, and mercury gas buret. The same Schlenk tube, stirrer, and stirring bar were used for all the hydrolysis experiments, which were run at the same stirring rate and temperature (21 °C). The results are shown in Figure 1.

Carbonylation of Wilkinson's Catalyst with $\text{CHCl}_3/\text{Alkali}$. A mixture of 40% KOH (5 g), CHCl_3 (5 mL), and $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ (0.104 g; 0.11 mmol) was vigorously stirred at 22 °C under nitrogen for 40 min. The yellow organic layer was separated and evaporated to give a thick, brownish yellow oil. Silica gel column chromatography of the oil (benzene as eluant) gave $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}]$ (25 mg; 32%), identified by comparison of spectral data (IR, ^{31}P NMR) with those of an authentic sample prepared from Wilkinson's catalyst and CO.²² IR (Nujol mull): ν_{CO} 1961 cm^{-1} . ^{31}P NMR (chloroform): δ 29.3 (d, $J(\text{P-Rh}) = 126$ Hz).

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