samples. Final concentrations of **7d** and thiophenol were determined by subtraction of the amount of product arising from each from the amount of starting materials.

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Registry No. **6a**, 111916-74-6; **6b**, 119368-34-2; **7a**, 119368-33-1; **7b**, 624-75-9; **7c**, 7425-55-0; **7d**, 623-48-3; **7e**, 29263-94-3; **7f**, 105-36-2; **8a**, 119391-50-3; **8b**, 7521-19-9; **8c**, 119368-35-3; **8d**, 28856-92-0; **9a**, 26891-70-3; **9b**, 119368-36-4; I_2, 7553-56-2; Br_2, 7726-95-6; $CH_3(CH_2)_9CH_2^{\bullet}$, 55101-35-4; $CH_3(CH_2)_6CH_2^{\bullet}$, 4606-96-6; octyl iodide, 629-27-6; octyl bromide, 111-83-1; undecyl bromide, 693-67-4; diethyl methylmalonate, 609-08-5; ethyl 2-bromo-2-methylpropanoate, 600-00-0.

Platinum Complex Catalyzed Carbonylation of Organic Iodides: Effective Carbonylation of Organic Iodides Having β-Hydrogens on Saturated sp^3 Carbons

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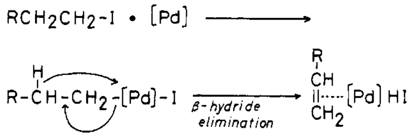
Dichlorobis(triphenylphosphine)platinum(II) is an effective catalyst precursor for the carbonylation of organic iodides having β-hydrogens on saturated sp^3 carbons. The carbonylation under carbon monoxide pressure in the presence of alcohol gives esters, and aldehydes are obtained by the reaction under carbon monoxide and hydrogen pressure. Thus, 1-iodohexane is carbonylated to methyl heptanoate in 79% yield in the presence of methanol at 120 °C under 70 kg cm^{-2} of initial carbon monoxide pressure. Heptanal is formed in 86% yield from 1-iodohexane at 120 °C under carbon monoxide (50 kg cm^{-2}) and hydrogen (50 kg cm^{-2}). Alkenyl and alkynyl iodides are also smoothly carbonylated in the presence of alcohol into the corresponding esters without reduction of unsaturated bonds.

Introduction

Transition-metal-catalyzed carbonylations of organic halides with carbon monoxide are valuable synthetic methods for the direct introduction of a carbonyl group into organic molecules and have been extensively studied.[1] Thus far, many transition-metal complexes such as iron,[2] cobalt,[3] nickel,[4] rhodium,[5] and palladium[6] are known to be active as catalysts. Among them, palladium complexes show high catalytic activity under mild reaction conditions and are very widely employed. Palladium complex catalyzed carbonylations of organic halides are extremely useful synthetic tools.[7] In the palladium-catalyzed reactions, however, there exists one major limitation. Applicable substrates are limited to organic halides such as aryl, alkenyl, benzyl, and allyl halides, since the intermediate (σ-organo)palladium species generated by oxidative addition of these halides to active metal centers do not undergo β-hydride elimination. On the other hand, in the case of organic halides having β-hydrogens on saturated sp^3 carbons, palladium catalysts do not afford carbonylated products effectively due to the β-hydride elimination of (σ-alkyl)palladium species (eq 1). Recently, Alper et al. employed a palladium–rhodium binary catalyst system with metal alkoxides as alkoxylating reagents to overcome this limitation.[8] However, the catalytic activity was not satisfactory. Besides palladium-catalyzed reactions, cobalt-catalyzed carbonylation of organic halides having β-hydrogens on sp^3 carbons has been reported.[9] However, the catalytic activity was quite low and rearranged prod-



(1)

Table I. Activities of Several Catalyst Precursors and Effect of Bases on the Methoxycarbonylation of 1-Iodohexane[a]

run	catalyst	base	conv,[b] %	yield,[c] %
1	$PtCl_2(PPh_3)_2$	K_2CO_3	97	75
2	$PtCl_2(PPh_3)_2$	NaOAc	26	2
3	$PtCl_2(PPh_3)_2$	Na_2CO_3	49	13
4	$PtCl_2(PPh_3)_2$	$NaHCO_3$	29	4
5	$Pt(CO)_2(PPh_3)_2$	K_2CO_3	100	73
6	$Pt(PPh_3)_4$	K_2CO_3	97	52
7	$PtCl_2(AsPh_3)_2$	K_2CO_3	69	39
8[d]	$PtCl_2(PCy_3)_2$	K_2CO_3	99	58
9[d]	$Pd(PPh_3)_4$	K_2CO_3	100	21
10[d]	$PdCl_2(PPh_3)_2$	K_2CO_3	90	5

[a] 1-Iodohexane (10 mmol), catalyst (0.50 mmol), base (12 mmol), methanol (40 mmol), and dioxane (15 mL) at 120 °C for 9 h under CO (initial pressure 70 kg cm^{-2}). [b] Conversion of 1-iodohexane determined by GLC, i.e., 100 × (1 − starting material recovered/starting material charged). [c] Yield of methyl heptanoate determined by GLC, i.e., 100 × (product formed/starting material charged). [d] K_2CO_3 (6.0 mmol), MeOH (60 mmol).

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ucts were obtained in some cases.

In this paper, we describe the full details on the platinum-catalyzed carbonylation of organic iodides.[10] This novel catalyst system achieves effective carbonylation of organic iodides having β-hydrogens on saturated sp^3 carbons, as well as the carbonylation of alkenyl and alkynyl iodides.

Results and Discussion

Carbonylation of Organic Iodides Having β-Hydrogens on Saturated sp^3 Carbon. Organic iodides having β-hydrogens on saturated sp^3 carbons are smoothly carbonylated in the presence of an alcohol and a catalytic amount of $PtCl_2(PPh_3)_2$. The reaction gave the corresponding esters at 120 °C in 9 h under 70 kg cm^{-2} of initial CO pressure (eq 2).

$$n\text{-}C_6H_{13}I + CO + MeOH \xrightarrow[K_2CO_3,\ -HI]{PtCl_2(PPh_3)_2} n\text{-}C_6H_{13}COOMe \qquad (2)$$

Activities of several catlyst precursors and effect of bases are examined in the carbonylation of 1-iodohexane (Table I). Among the platinum complexes, $PtCl_2(PPh_3)_2$ and $Pt(CO)_2(PPh_3)_2$ showed high catalytic activity to give methyl heptanoate in 75% and 73% yields (runs 1 and 5). Under the present reaction conditions, $PtCl_2(PPh_3)_2$ is reduced in situ to $Pt(CO)_2(PPh_3)_2$ judging from FT-IR measurement (1990 and 1950 cm^{-1}) of the resulting reaction mixture ($Pt(CO)_2(PPh_3)_2$; lit.[11] 1990 and 1948 cm^{-1}). Other di- and zerovalent platinum complexes were less effective (runs 6–8). In the present carbonylation, palladium catalysts such as $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ were totally unsatisfactory in terms of yields and selectivites (runs 9 and 10). Furthermore, after the reaction, palladium metal was always deposited in these cases.

In this carbonylations, a base was indispensable to scavenge hydrogen iodide generated in the reaction and the nature of the base affected the reaction markedly. Organic bases such as tertiary amines easily reacted with organic iodides to give quaternary ammonium salts prior to the carbonylation. Even 1,8-bis(dimethylamino)naphthalene (Proton Sponge), which is a very strong base with pK_a 12.34 and only weakly nucleophilic,[12] was not effective in the present reaction. So, several inorganic bases were examined in the reaction. Among inorganic bases tried, only K_2CO_3 was effective (run 1). Other inorganic bases such as NaOAc, Na_2CO_3, and $NaHCO_3$ did not give good results (runs 2–4).

Table II. Effect of an Amount of Methanol on the Methoxycarbonylation of 1-Iodohexane[a]

run	MeOH/mmol	conv,[b] %	yield,[c] %
11	20	98	61
1	40	97	75
12[d]	60	99	79
13	120	100	5
14[e]	370	100	0
15[f]	40	98	72
16[g]	40	83	48

[a] 1-Iodohexane (10 mmol), methanol, $PtCl_2(PPh_3)_2$ (0.50 mmol), K_2CO_3 (12 mmol), and dioxane (15 mL) at 120 °C for 9 h under CO (70 kg cm^{-2}). [b] Conversion of 1-iodohexane determined by GLC. [c] Yield of methyl heptanoate determined by GLC. [d] K_2CO_3 (6.0 mmol). [e] In methanol (370 mmol, 15 mL), without dioxane. [f] THF (15 mL) in place of dioxane. [g] Benzene (15 mL) in place of dioxane.

Table III. Alkoxycarbonylation of Various Organic Iodides[a]

run	iodide	product	yield,[b] %
17[c]	$n\text{-}C_{10}H_{21}I$	$n\text{-}C_{10}H_{21}COOMe$	68
18	$C_6H_5(CH_2)_2I$	$C_6H_5(CH_2)_2COOMe$	56
19[d]	cyclo-$C_6H_{11}I$	cyclo-$C_6H_{11}COOMe$	74[e]
20[f]	$n\text{-}C_6H_{13}CH(CH_3)I$	$n\text{-}C_6H_{13}CH(CH_3)COOMe$	76[e]
21	$(E)\text{-}C_2H_5CH{=}CHC_2H_4I$	$(E)\text{-}C_2H_5CH{=}CHC_2H_4COOMe$	65
22	$(Z)\text{-}C_2H_5CH{=}CHC_2H_4I$	$C_2H_5CH{=}CHC_2H_4COOMe$	66[e,g]
23	C_6H_5I	$C_6H_5\text{-}COOMe$	57
24[h]	$n\text{-}C_6H_{13}I$	$n\text{-}C_6H_{13}COO\text{-}n\text{-}C_6H_{13}$	71
25[i]	$n\text{-}C_6H_{13}I$	$n\text{-}C_6H_{13}COOCH(CH_3)C_2H_5$	62

[a] Organic iodide (10 mmol), $PtCl_2(PPh_3)_2$ (0.50 mmol), K_2CO_3 (6.0 mmol), methanol (60 mmol), and dioxane (15 mL) at 120 °C for 9 h under CO (70 kg cm^{-2}). [b] Determined by GLC. [c] Methanol (120 mmol). [d] Methanol (40 mmol). [e] Isolated yield. [f] THF (15 mL). [g] $Z{:}E$ = 4:1. [h] 1-Hexanol was used in place of methanol. [i] 2-Butanol was used in place of methanol.

Methanol has a significant influence on the present carbonylation (Table II). When a 4–6 molar excess of methanol was used with dioxane as a cosolvent, the yield of the ester reached a maximum (runs 1 and 12). As the amount of methanol increased, the yield of ester decreased drastically (run 13). When the reaction was performed in a large excess of methanol (37 equiv and without cosolvent), the ester was not obtained at all (run 14). Tetrahydrofuran and benzene also can be used as a cosolvent (runs 15 and 16).

Both the reaction temperature and CO pressure also affect the reaction considerably. When the reaction was carried out at 150 °C, selectivity to the ester decreased considerably and the yield of the ester was 40%. At 95 °C, conversion of 1-iodohexane was lowered to 34% and the yield of the ester was only 9%. Lower initial CO pressure somewhat reduced the yield of ester (60% at 30 kg cm^{-2} of initial CO pressure).

Various organic iodides were alkoxycarbonylated with the present catalyst system (Table III). 1-Iododecane and

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Table IV. Effect of Pressure and Composition of Synthesis Gas on the Formylation of 1-Iodohexane[a]

run	CO, kg cm^{-2}	H_2, kg cm^{-2}	conv,[b] %	yield,[c] %
26	50	50	99	86
27	30	30	75	47
28	70	30	94	81
29	30	70	55	31

[a] 1-Iodohexane (10 mmol), $PtCl_2(PPh_3)_2$ (0.50 mmol), K_2CO_3 (12 mmol), and dioxane (15 mL) at 120 °C for 9 h. [b] Conversion of 1-iodohexane determined by GLC. [c] Yield of heptanal determined by GLC.

β-phenethyl iodide gave the corresponding esters in good yields (runs 17 and 18). Cyclic and acyclic secondary iodides were also smoothly carbonylated to the corresponding esters (runs 19 and 20). (*E*)-1-Iodo-3-hexene gave (*E*)-methyl 4-heptenoate exclusively (run 21). On the other hand, (*Z*)-1-iodo-3-hexene gave a mixture of (*Z*)- and (*E*)-methyl 4-heptenoate (*Z*:*E* = 4:1) in 66% yield (run 22). The following observations clearly indicate that this *Z*/*E* ratio reflects the thermodynamic stability of the products. Namely, during the reaction, the carbonylated product (*Z*)-methyl 4-heptenoate was isomerized to the *E* isomer; *Z*:*E* was 6:1 after 6 h (total isolate yield 46%) and 4:1 after 9 h (total isolated yield 66%). Furthermore, under the reaction conditions, the starting materials, (*Z*)- and (*E*)-1-iodo-3-hexene, were not isomerized to each other al all. Iodobenzene was also carbonylated to give the corresponding ester (run 23). As mentioned above, primary and secondary alkyl iodides are effectively carbonylated in the present reaction. However, tertiary alkyl iodides such as *tert*-butyl iodide and 2-iodo-2-methyloctane could not be carbonylated because of dehydrohalogenation prior to the carbonylation.

In place of methanol, 1-hexanol and 2-butanol can also be used and gave the corresponding esters in good yields (runs 24 and 25). In palladium-catalyzed carbonylation of aryl halides, secondary alcohols favored the double carbonylation.[13] In the present platinum-catalyzed reaction, however, no α-keto esters were found even in the presence of secondary alcohol. With tertiary alcohols (2-methyl-2-propanol) or less nucleophilic alcohol (2,2,2-trifluoroethanol), the carbonylation did not proceed at all.

The present platinum catalyst system can be applied to efficient formylation of alkyl iodides. Under the pressure of carbon monoxide and hydrogen (synthesis gas), organic iodides having β-hydrogens on saturated sp^3 carbons are smoothly formylated to give the corresponding aldehydes in good yields (eq 3).

$$n\text{-}C_6H_{13}I + CO + H_2 \xrightarrow[K_2CO_3,\ -HI]{PtCl_2(PPh_3)_2} n\text{-}C_6H_{13}CHO \qquad (3)$$

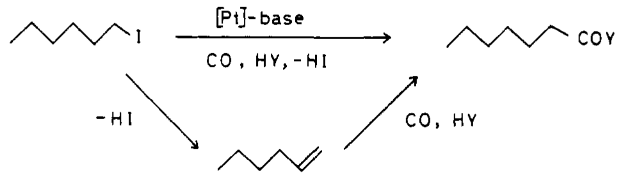
The yields of the aldehyde are influenced by partial pressure of carbon monoxide and hydrogen as shown in Table IV. Under total initial pressure of 100 kg cm^{-2} (CO/H_2 = 1/1 or 7/3), heptanal was obtained in high yields (runs 26 and 28). Under lower total initial pressure (total 60 kg cm^{-2}, CO/H_2 = 1/1) or higher hydrogen partial pressure (total 100 kg cm^{-2}, CO/H_2 = 3/7), the yield of the aldehyde was reduced (runs 27 and 29). When other hydride sources such as HCOOK, HCOONa, and $HCOONH_4$ instead of molecular hydrogen were used, the aldehyde was not obtained at all.

Table V. Formylation of Various Organic Iodides[a]

run	iodide	product	yield,[b] %
26	n-$C_6H_{13}I$	n-$C_6H_{13}CHO$	86
30	n-$C_{10}H_{21}I$	n-$C_{10}H_{21}CHO$	61
31	$C_6H_5(CH_2)_2I$	$C_6H_5(CH_2)_2CHO$	53
32	cyclo-$C_6H_{11}I$	cyclo-$C_6H_{11}CHO$	78
33	n-$C_6H_{13}CH(CH_3)I$	n-$C_6H_{13}CH(CH_3)CHO$	51

[a] Organic iodide (10 mmol), $PtCl_2(PPh_3)_2$ (0.50 mmol), K_2CO_3 (12 mmol), and dioxane (15 mL) at 120 °c for 9 h under CO (50 kg cm^{-2}) and H_2 (50 kg cm^{-2}). [b] Determined by GLC.

Scheme I

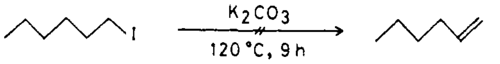


(Y = -OR,-H)

Various organic iodides are effectively formylated by this procedure under CO/H_2 pressure (Table V). 1-Iodoalkanes such as 1-iododecane and β-phenethyl iodide gave the corresponding aldehydes in good yields (runs 30 and 31). Cyclic and acyclic secondary iodides such as iodocyclohexane and 2-iodooctane were also smoothly formylated (runs 32 and 33).

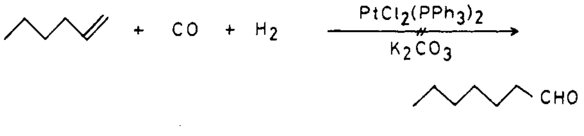
In the present alkoxycarbonylation and formylation reactions, the iodides are directly replaced by alkoxycarbonyl or formyl functionalities, and no other regioisomers are obtained. This feature is very important, since in hydroesterification or hydroformylation of olefins[14] two regioisomers are inevitably formed.

There exists some possibility that the carbonylation occurs after an elimination of hydrogen iodide from the substrates (Scheme I). Namely, hydroesterification or hydroformylation of olefins generated from organic iodides might be operative. Knifton has reported that the platinum complex showed a high catalytic activity in the hydroesterification of olefins.[15] Under the present reaction conditions, however, the elimination of hydrogen iodide from 1-iodohexane did not occur even in the presence of a stoichiometric amount of K_2CO_3 (eq 4; the conversion



(4)

of 1-iodohexane was 6.1%). Furthermore, 1-hexene in place of 1-iodohexane did not give the hydroformylated product in the presence of the platinum catalyst under the CO/H_2 pressure (eq 5; see Experimental Section). These results exclude the possibility of Scheme I.



(5)

The most plausible catalytic cycle is illustrated in Scheme II. Oxidative addition of organic iodides to the active platinum center would afford the (σ-alkyl)platinum intermediate. Insertion of CO into the alkyl–platinum

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Table VI. Methoxycarbonylation of (*E*)- and (*Z*)-1-Iodo-1-octene[a]

run	iodide	condtn[b]	catalyst	CO, kg cm^{-2}	base	temp, °C	time, h	conv,[c] %	yield,[d] %
34	*E*	A	$Pt(CO)_2(PPh_3)_2$	30	K_2CO_3	100	7	92	80 (0/100)
35	*E*	A	$Pt(CO)_2(PPh_3)_2$	70	K_2CO_3	100	7	94	81 (0/100)
36	*E*	A	$PtCl_2(PPh_3)_2$	1	Et_3N	80	8	43	22 (0/100)
37	*E*	B	$PtCl_2(PPh_3)_2$	1	Et_3N	80	6	88	73 (0/100)
38	*Z*	A	$PtCl_2(PPh_3)_2$	30	Et_3N	100	24	99	87 (79/21)
39	*Z*	A	$PtCl_2(PPh_3)_2$	30	K_2CO_3	100	24	97	76 (68/32)
40	*Z*	B	$PtCl_2(PPh_3)_2$	1	Et_3N	80	8	35	31 (87/13)

[a] n-$C_6H_{13}CH{=}CHI$ (2.5 mmol), platinum complex (0.125 mmol). [b] A, MeOH (22.5 mmol), base (3.0 mmol), 1,4-dioxane (3.8 mL); B, MeOH (3.0 mL), Et_3N (3.0 mL). [c] Conversion of 1-iodo-1-octene determined by GLC. [d] Yield of methyl 2-nonenoate determined by GLC. Figures in parentheses are the ratio of *Z*/*E*.

Scheme II

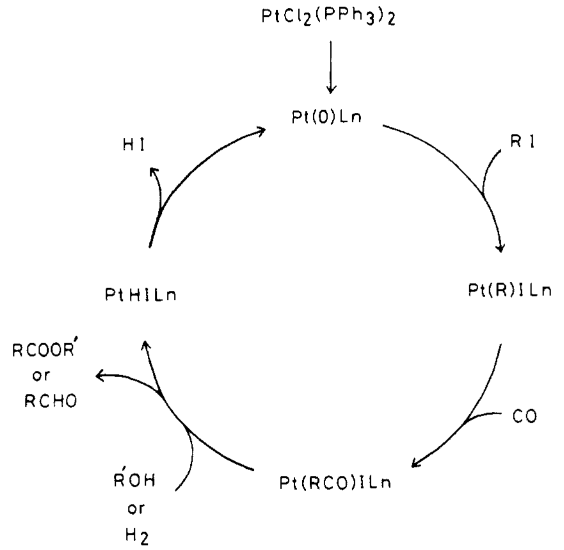

Table VII. Methoxycarbonylation of 1-Iodo-1-octyne under Various Reaction Conditions[a]

run	CO, kg cm^{-2}	temp, °C	yield,[b] %
41	1	60	0[c]
42	20	60	56
43	30	60	54
44	80	60	40
45	30	40	3
46	30	90	0

[a] n-$C_6H_{13}C{\equiv}CI$ (5.0 mmol), $PtCl_2(PPh_3)_2$ (0.25 mmol), Et_3N (6.0 mmol), MeOH (45 mmol), and 1,4-dioxane (7.6 mL) were stirred for 6 h under carbon monoxide pressure. [b] Yield of methyl 2-nonynoate determined by GLC. Conversion of 1-iodo-1-octyne was 100%. [c] 7,9-Hexadecadiyne was obtained in 59% yield.

bond followed by nucleophilic attack of alcohol or hydrogenolysis with molecular hydrogen provides the esters and aldehydes.[16] Then, base-assisted elimination of hydrogen iodide allows a catalytic cycle to be closed by regenerating an active platinum species. The key intermediate in the reaction appears to be a (σ-alkyl)platinum species. Compared with (σ-alkyl)palladium species, the platinum analogues are rather stable[18] and will not undergo β-hydride elimination prior to carbon monoxide insertion. This property of the platinum intermediate would facilitate the successful carbonylation of the organic iodides having β-hydrogens on saturated sp^3 carbons.

In the present reaction, only organic iodides could be used as the substrates. The corresponding bromides were not carbonylated at all. In the presence of KI (1 equiv), however, 1-bromohexane was methoxycarbonylated to methyl heptanoate in 36% yield; conversion of 1-bromohexane was 95% and 1-iodohexane was also obtained in 16% yield (see Experimental Section). These results indicated that the bromide was converted to the corresponding iodide in situ and the carbonylation of this iodide proceeded.

Carbonylation of Alkenyl Iodides. Carbonylation of alkenyl halides,[6] as well as aryl, benzyl, and allyl halide, has been well-studied commonly with palladium catalyst. The present platinum complex system is also effective for the carbonylation of alkenyl iodides (Table VI). Both organic and inorganic bases could be employed in this carbonylation. (*E*)-1-Iodo-1-octene is carbonylated exclusively to (*E*)-methyl 2-nonenoate in good yield. In the presence of a small excess (1.2 equiv) of base (condition A), a CO initial pressure higher than 30 kg cm^{-2} is necessary to give the esters in good yields (runs 34–36). On the other hand, when a large excess of Et_3N (8.6 equiv) was employed (condition B), the carbonylation proceeded under an even atmospheric pressure of carbon monoxide (balloon) (run 37). The same phenomenon was observed in palladium-catalyzed carbonylations.[6]

(*Z*)-1-Iodo-1-octene was also carbonylated to the corresponding ester by the present catalyst system although the product was a mixture of the *Z* and *E* ester (runs 38 and 39). Contrary to the *E* isomer (run 37), the carbonylation was very sluggish under an atmospheric pressure of carbon monoxide (run 40).

Carbonylation of Alkynyl Iodides. Carbonylation of acetylenic compounds have been well-studied.[1e] Acetylenic compounds, however, are so reactive that it is rather difficult to control the reactions.[1e] In carbonylation of terminal acetylenes, the triple bond was frequently reduced to a double bond and α,β-unsaturated carboxylic acid derivatives were usually obtained.[19] We also reported platinum complex catalyzed carbonylation of acetylenic compounds.[20] To our knowledge, there is only one ex-

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[16] There may be an alternative possibility that the present carbonylation reactions proceed via (alkoxycarbonyl)- or formylplatinum species as intermediates (eq 8 and 9). Reductive elimination of RCOOR'

$$L_nPt(R)(I)(CO) + R'OH \xrightarrow[-HI]{} L_nPt(R)(COOR') \qquad (8)$$

$$L_nPt(R)(I)(CO) + H_2 \xrightarrow[-HI]{} L_nPt(R)(CHO) \qquad (9)$$

or RCHO can give esters or aldehydes as the products. However, it is well-known that formyl transition-metal species are thermodynamically unstalbe and equilibriums lie far toward hydridocarbonyl, not formyl, species.[17] Therefore, provided the same mechanism is operating for the present alkoxycarbonylation and formylation reactions, the alkoxycarbonyl and the formyl intermediacies depicted in eq 8 and 9 seem unlikely.

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Table VIII. Activities of Several Catalyst Precursors and Effect of Bases on the Methoxycarbonylation of 1-Iodo-1-octyne[a]

run	catalyst	base	conv,[b] %	yield,[c] %
43	$PtCl_2(PPh_3)_2$	Et_3N	100	54
47	$Pt(CO)_2(PPh_3)_2$	Et_3N	100	40
48[d]	$PtCl_2(PhCN)_2$	Et_3N	100	49
49	$Pt(PPh_3)_4$	Et_3N	100	19
50[e]	$PtCl_2(PPh_3)_2$	K_2CO_3	74	5
51	$PtCl_2(PPh_3)_2$	pyridine	35	3
52	$PdCl_2(PPh_3)_2$	Et_3N	100	16

[a] n-$C_6H_{13}C{\equiv}CI$ (5.0 mmol), MeOH (45 mmol), catalyst (0.25 mmol), base (6.0 mmol), and 1,4-dioxane (7.6 mL) were stirred at 60 °C for 6 h under carbon monoxide (30 kg cm^{-2}). [b] Conversion of 1-iodo-1-octyne determined by GLC. [c] Yield of methyl 2-nonynoate determined by GLC. [d] $P(n\text{-}Bu)_3$ (0.60 mmol) was added. [e] K_2CO_3 (3.0 mmol) was used.

ample where the carbonylation reaction does not involve triple-bond reduction.[21] Furthermore, there is no precedent for the carbonylation reaction of alkynyl halides. The present $PtCl_2(PPh_3)_2$–Et_3N system showed a high catalytic activity in direct conversion of alkynyl iodides into acetylenecarboxylic acid esters without triple-bond reduction (eq 6).

$$n\text{-}C_6H_{13}C{\equiv}CI + CO + MeOH \xrightarrow[Et_3N,\ -HI]{PtCl_2(PPh_3)_2} n\text{-}C_6H_{13}C{\equiv}CCOOMe \qquad (6)$$

Table VII lists the results of the carbonylation of 1-iodo-1-octyne catalyzed by a $PtCl_2(PPh_3)_2$–Et_3N system. Under an atmospheric pressure of carbon monoxide, the carbonylation did not occur at all. Instead, 7,9-hexadecadiyne, homocoupling product of 1-iodo-1-octyne, was obtained in 59% yield (run 41, eq 7). With an increase

$$2\ n\text{-}C_6H_{13}C{\equiv}CI \xrightarrow[\substack{CO(1\,atm)\ \text{or}\ Ar\\ -2\,I}]{[Pt]-Et_3N} n\text{-}C_6H_{13}C{\equiv}C\text{-}C{\equiv}CC_6H_{13}\text{-}n \qquad (7)$$

in the carbon monoxide pressure, the yield of the carbonylated product increased. Under 20 kg cm^{-2} of initial carbon monoxide pressure, methyl 2-nonynoate was obtained in 56% yield together with 1-hexyne (10%) and 7,9-hexadecadiyne (1%) as byproducts (run 42). Higher carbon monoxide pressure somewhat suppressed the carbonylation (run 44). The reaction temperature is also critical. Below 40 °C or higher than 90 °C, the yields of the ester were drastically reduced (runs 45 and 46), whereas at 60 °C the yield of ester reached 56%.

Activities of several platinum and palladium complexes as well as effect of bases were summarized in Table VIII. $PtCl_2(PPh_3)_2$ gave the best result. $Pt(CO)_2(PPh_3)_2$ and $PtCl_2(PhCN)_2$–$P(n\text{-}Bu)_3$ also showed good catalytic activities and gave methyl 2-nonynoate in 40% and 49% yields (runs 47 and 48), whereas $Pt(PPh_3)_4$ was less effective (run 49). As for the bases, Et_3N was the most effective, while K_2CO_3 and pyridine reduced the catalytic activity considerably (runs 50 and 51). The palladium analogue, $PdCl_2(PPh_3)_2$, was not effective and both yield and selectivity of the ester were quite low (run 52).

2-Propanol can be used in place of methanol and 1-methylethyl 2-nonynoate was isolated in 29% yield. 1-Iodo-2-phenylethyne can be also carbonylated under the same reaction conditions as run 43 and gave the corresponding ester, methyl 3-phenyl-2-ethynoate in 33% yield. However, alkynyl bromide such as 1-bromo-2-phenylethyne did not react at all under the present reaction conditions, reminiscent of the no reactivity of the alkyl bromides in the present reaction (vide supra).

Conclusion

In this study, we have developed novel platinum catalyst systems, which show good activities for the carbonylation of alkyl, alkenyl, and alkynyl iodides under carbon monoxide pressure. Noteworthy is that the present platinum catalyst systems successfully overcome the limitation of the substrates and realize the effective carbonylation of organic iodides having β-hydrogens on saturated sp^3 carbons to give the corresponding esters and aldehydes without β-hydride elimination.

Experimental Section

Materials. The reagents employed in this study were dried and purified before use by the usual procedures. Carbon monoxide (>99.9%) was used without further purification. $PtCl_2(PPh_3)_2$,[22] $PtCl_2(AsPh_3)_2$,[23] $PtCl_2(PCy_3)_2$,[24] $Pt(CO)_2(PPh_3)_2$,[25] $Pt(PPh_3)_4$,[26] $Pd(PPh_3)_4$,[27] and $PdCl_2(PPh_3)_2$[28] were prepared by the literature methods. 1-Iodohexane and iodocyclohexane were commercial materials. (*E*)-1-Iodo-3-hexene, (*Z*)-1-iodo-3-hexene, 2-iodooctane, 1-iodooctane, and β-phenethyl iodide were prepared by the literature method[29] from the corresponding alcohols. (*E*)-1-Iodo-1-octene,[30] (*Z*)-1-iodo-1-octene,[31] 1-iodo-1-octyne,[31] and 1-iodo-2-phenylethyne[32] were prepared according to the literature.

General Procedure. A 100-mL stainless steel autoclave (Nitto Koatsu; SUS 316) equipped with a magnetically driven stirrer was used. A glass liner was set in the autoclave and the inside of the autoclave was heated by a heat gun (400 W) for 2 min. After cooling under an argon stream, the reagents were charged in the following order: solvent (15 mL), alcohol (60 mmol), organic iodide (10 mmol), K_2CO_3 (6.0 mmol), $PtCl_2(PPh_3)_2$ (0.50 mmol). After sealing and flushing with carbon monoxide, the reactor was pressured with carbon monoxide to 70 kg cm^{-2}. The autoclave was heated to 120 °C in 10 min and held at this temperature for 9 h. The reaction was terminated by rapid cooling and the autoclave was discharged. The resulting brown solution was analyzed with GLC. The products were isolated by vacuum distillation. The identification of the products was confirmed by IR, ^1H and ^{13}C NMR, elemental analyses, and GC-MS. The boiling points are uncorrected. The GLC analyses were carried out with Shimadzu GC-4CM and GC-8A chromatographs equipped with columns (3 mm × 3 m) packed with PEG-HT (5% on Uniport HP, 60–80 mesh), Silicone OV-17 (2% on chromosorb W(AW-DMCS), 80–100 mesh), and Apiezon grease L (5% on Neopack 1A, 60–80 mesh). The IR spectra were measured on a Nicolet 5MX Fourier transform infrared spectrophotometer. The ^{13}C NMR and ^1H NMR spectra were recorded at 25.05 and 100 MHz, respectively, with a JEOL JNM FX 100 spectrometer. ^1H NMR spectra (300 MHz) were recorded on a Nicolet NTC-300 spectrometer equipped with a 1180E computer system. Samples were dissolved in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Mass spectra (MS) were obtained on a Shimadzu QP-1000 spectrometer.

For products other than listed below, all the spectral (^1H and ^{13}C NMR, and IR) data were consistent with those of authentic samples.

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Hydroformylation of 1-Hexene in Place of 1-Iodohexane (eq 5). A mixture of 1-hexene (9.4 mmol), $PtCl_2(PPh_3)_2$ (0.50 mmol), K_2CO_3 (6.0 mmol), and dioxane (15 mL) was placed in a 100-mL stainless steel autoclave. The reactor was pressured with carbon monoxide (50 kg cm^{-2}) and molecular hydrogen (50 kg cm^{-2}) and stirred at 120 °C for 9 h. No carbonylated products were detected by GLC and IR measurements.

Carbonylation of 1-Bromohexane in the Presence of Potassium Iodide. A mixture of 1,4-dioxane (7.6 mL), methanol (30 mmol), 1-bromohexane (5.0 mmol), K_2CO_3 (3.0 mmol), $PtCl_2(PPh_3)_2$ (0.25 mmol), and potassium iodide (5.5 mmol) was placed in a 50-mL stainless steel autoclave (Yuasa Giken; SUS 304) equipped with a glass liner and a magnetic stirring bar. The reactor was pressured with carbon monoxide to 70 kg cm^{-2} and stirred at 120 °C for 9 h.

(*E*)- and (*Z*)-methyl 4-heptenoate: colorless oil; bp 86–88 °C (37 mmHg); IR (neat) 1742 cm^{-1} (C=O); ^{1}H NMR (300 MHz) ($CDCl_3$) δ 0.96 (t, 3 H, CH_3, J = 7.5 Hz), 2.06 (quintet, 2 H, CH_2CH_3, J = 7.5 Hz), 2.35 (m, 2 H, -CH_2-), 2.36 (m, 2 H, -CH_2-), 3.67 (s, 3 H, OCH_3), 5.25–5.55 (m, 2 H, -CH=CH-); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.27 (q, CH_3), 20.49 (t, CH_2CH_3(*Z*)), 22.72 (t, CH_2CH=(*Z*)), 25.54 (t, CH_2CH_3(*E*)), 27.89 (t, CH_2CH=(*E*)), 34.23 (t, CH_2COOMe), 51.48 (q, OCH_3), 126.70 (d, —CH=), 133.16 (d, -CH=), 173.61 (s, C=O). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92; O, 22.50. Found: C, 67.39; H, 10.07; O, 22.25.

Methyl 2-nonynoate: IR (neat) 1721 cm^{-1} (C=O); ^{1}H NMR (90 MHz) ($CDCl_3$) δ 0.89 (t, 3 H, CH_3), 1.02–1.73 (m, 8 H, —CH_2—), 2.34 (t, 2 H, —$CH_2C\equiv$), 3.76 (s, 3 H, OCH_3); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.03 (q, CH_3), 18.67 (t, —CH_2—) 22.54 (t, —CH_2—), 27.59 (t, —CH_2—), 28.59 (t, —CH_2—), 31.29 (t, —CH_2—), 52.43 (q, OCH_3), 72.98 (s, $C\equiv CCO$), 89.77 (s, —$C\equiv CCO$—), 154.17 (s, C=O).

Isopropyl 2-nonynoate: ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 13.97 (q, CH_3), 18.67 (t, —CH_2—), 21.66 (q, $CH(CH_3)_2$), 22.49 (t, —CH_2—), 27.59 (t, —CH_2—), 28.53 (t, —CH_2—), 31.23 (t, —CH_2—), 69.45 (d, —CO_2CH), 73.56 (s, $C\equiv CCO$), 88.83 (s, $C\equiv CCO$), 153.35 (s, C=O).

7,9-Hexadecadiyne: colorless oil; bp 130 °C (0.08 mmHg); ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.89 (t, 6 H, 2 CH_3), 1.01–1.52 (m, 16 H, —CH_2—), 2.24 (t, 4 H, 2 —$CH_2C\equiv$); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 14.03 (q, CH_3), 19.25 (t, —CH_2—), 22.56 (t, —CH_2—), 28.41 (t, —CH_2—), 28.56 (t, —CH_2—), 31.33 (t, —CH_2—), 65.35 (s, —$C\equiv CC\equiv C$—), 77.48 (s, —$C\equiv CC\equiv C$—); MS, m/z 218.

Methyl 3-phenyl-2-propynoate: colorless oil; bp 130 °C (3 mmHg); IR (neat) 1717 cm^{-1} (C=O); ^{13}C NMR (25.05 MHz) ($CDCl_3$) δ 52.72 (q, OCH_3), 80.37 (s, $PhC\equiv C$), 86.42 (s, $\equiv CCO_2$—), 119.53 (s, phenyl 1), 128.52 (d, phenyl 2,6), 130.63 (d, phenyl 4), 132.92 (d, phenyl 3,5), 154.40 (s, C=O). Anal. Calcd for $C_{10}H_8O_2$: C, 75.0; H, 5.0; O, 20.0. Found: C, 74.47; H, 5.22; O, 20.11.

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Registry No. $PtCl_2(PPh_3)_2$, 10199-34-5; $Pt(CO)_2(PPh_3)_2$, 15377-00-1; $Pt(PPh_3)_4$, 14221-02-4; $PtCl_2(AsPh_3)_2$, 16242-55-0; $PtCl_2(PCy_3)_2$, 60158-99-8; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2(PPh_3)_2$, 13965-03-2; $PtCl_2(PhCN)_2$, 14873-63-3; $C_{10}H_{21}I$, 2050-77-3; $C_6H_5(CH_2)_2I$, 17376-04-4; cyclo-$C_6H_{11}I$, 626-62-0; $C_6H_{13}CH(CH_3)I$, 557-36-8; (*E*)-$C_2H_5CH{=}CHC_2H_4I$, 119245-02-2; (*Z*)-$C_2H_5CH{=}CHC_2H_4I$, 21676-03-9; C_6H_5I, 591-50-4; $C_6H_{13}I$, 638-45-9; $C_{10}H_{21}CO_2Me$, 1731-86-8; $C_6H_5(CH_2)_2CO_2Me$, 103-25-3; cyclo-$C_6H_{11}CO_2Me$, 4630-82-4; $C_6H_{13}CH(CH_3)CO_2Me$, 2177-86-8; (*E*)-$C_2H_5CH{=}CHC_2H_4CO_2Me$, 54004-29-4; (*Z*)-$C_{H5}CH{=}CHC_2H_4CO_2Me$, 39924-30-6; $C_6H_5CO_2Me$, 93-58-3; $C_6H_{13}CO_2C_6H_{13}$, 1119-06-8; $C_6H_{13}CO_2CH(CH_3)C_2H_5$, 119245-03-3; $C_6H_{13}CHo$, 111-71-7; $C_6H_{21}CHO$, 112-44-7; $C_6H_5(CH_2)_2CHO$, 104-53-0; cyclo-$C_6H_{11}CHO$, 2043-61-0; $C_6H_{13}CH(CH_3)CHO$, 7786-29-0; $C_6H_{13}C\equiv CI$, 81438-46-2; $IC\equiv CC_6H_5$, 932-88-7; 1-hexene, 592-41-6; 1-bromohexane, 111-25-1; methyl 2-nonynoate, 111-80-8; isopropyl 2-nonynoate, 119245-04-4; 7,9-hexadecadiyne, 18277-20-8; methyl 3-phenyl-2-propynoate, 4891-38-7; methyl heptanoate, 106-73-0; (*E*)-1-iodo-1-octene, 42599-17-7; (*Z*)-1-iodo-1-octene, 52356-93-1; (*E*)-methyl nonenoate, 14952-06-8; (*Z*)-methyl nonenoate, 68872-72-0.

Substitution Reactions in the β-Styryl and Phenylethynyl Systems[1]

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Substitution for Q in the systems $PhCH{=}CHQ$, $Ph_2C{=}CHQ$, and $PhC\equiv CQ$ can occur by a free-radical chain mechanism where the attacking radical is alkyl (Q = HgX, Bu_3Sn, $PhSO_2$, PhSO, PhS, Cl, Br, I) or $(EtO)_2PO^\bullet$ (Q = HgX, Bu_3Sn, I). The $Q^\bullet$ radicals formed by β-elimination can generate t-$Bu^\bullet$ or $(EtO)_2PO^\bullet$ by reaction with t-BuHgCl, $Hg[P(O)(OEt)_2]_2$, $ClHg[P(O)(OEt)_2]$ or by electron transfer between $^\bullet$HgCl and $(EtO)_2PO^-$. With Q = PhS or $PhSO_2$, relative reactivity data indicates that the free radical addition–elimination sequence occurs for t-BuLi at 0 or 45 °C and that this process may also be involved in reactions of t-BuMgCl or *tert*-butyl cuprates with some of the substrates. Ionic reaction of $(EtO)_2PO^-$ with the three substrates with Q = $PhSO_2$ or halogen are examined. With Q = $PhSO_2$, $PhCH[P(O)(OEt)_2]CH_2P(O)(OEt)_2$, $Ph_2C{=}CHP(O)(OEt)_2$, and $PhC\equiv CP(O)(OEt)_2$ are formed in good yield.

Substitution at an unsaturated carbon atom can occur by the addition–elimination of either nucleophiles or radicals. Alkyl substitution for a variety of electronegative or electropositive substituents in the β-styryl or phenylethynyl system occurs by the free-radical chain mechanism as shown in Scheme I in a photostimulated reaction with alkylmercury halides.[2] In the present paper, we summarize the results of this homolytic process with t-BuHgCl and examine the possibility of homolytic processes being involved in the reactions of other organometallic reactions and in the reactions involving $(EtO)_2PO^-$ as a nucleophile, where the course of the reaction depends upon the structure of the substrate and the nature of the leaving group.

Scheme I

$$R^\bullet + QCH{=}CHPh \rightarrow R(Q)CH\dot{C}HPh$$

$$R(Q)CH\dot{C}HPh \rightarrow RCH{=}CHPh + Q^\bullet$$

$$Q^\bullet + RHgCl \rightarrow R^\bullet + QHgCl$$

Summary of Reactions with *tert*-Butylmercury Chloride. For substitution by an alkyl radical, the leaving group Q in 1–3 can be HgX, Bu_3Sn, $PhSO_2$, PhSO, PhS, Cl, Br, or I.[2-7] The eliminated radical $Q^\bullet$ will regenerate

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