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Photo-, electro-, and thermal carbonylation of alkyl iodides in the presence of Group 7 and 8–10 metal carbonyl catalysts

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Abstract

Various transition-metal complexes including Group 7 and 8–10 metal carbonyls are highly active catalyst precursors for the photochemical carbonylation of alkyl iodides having β-hydrogens on saturated sp^3-carbons at room temperature under 1 atm of carbon monoxide. Primary, secondary and tertiary alkyl iodides are smoothly carbonylated by this catalyst system without β-hydride elimination (dehydrohalogenation) to give the corresponding esters or amides in high yields. In employment of $Mn_2(CO)_{10}$ as a catalyst, electrochemical carbonylation of alkyl iodides also occurred via generation of an anionic manganese carbonyl intermediate. Actually, anionic manganese carbonyl complexes (pentacarbonylmanganates) showed high catalytic activity for thermal carbonylation of alkyl iodides at room temperature under 1 atm of carbon monoxide without photo-irradiation and electrolysis. Mechanistic studies were performed with kinetics and ESR and it was suggested that the present photo-, electro- and thermal carbonylation would involve a non-chain radical mechanism.

Key words: Group 7; Group 8; Group 9; Group 10; Carbonylation; Catalysis; Alkyl iodide

1. Introduction

The scope and understanding of carbonylation has grown to such an extent that it can now be regarded, like catalytic hydrogenation, as one of the more generally useful techniques of synthetic organic chemistry [1]. However, even after continuous development of carbonylation chemistry, carbonylation of alkyl halides having β-hydrogens on saturated sp^3-carbons by transition-metal catalysts remains unsolved and a new methodology for catalytic carbonylation of alkyl halides is required [2]. We have recently reported the first, and simple, platinum complex-catalyzed thermal carbonylation of various organic iodides involving alkyl halides [3,4]. It was considered that this reaction is characteristic of platinum complexes because of the exceptional stability of σ-alkyl platinum intermediates [5]. These reactions, however, required relatively high reaction temperature and carbon monoxide pressure (*i.e.*, at 120°C under 70 kg cm^{-2} of carbon monoxide) [3]. In the course of our further study, we found that not only platinum complexes but also Group 7 and 8–10 metal carbonyls effectively catalyzed the photochemical carbonylation of alkyl iodides having β-hydrogens on saturated sp^3-carbons under extremely mild reaction conditions (at room temperature under 1 atm of carbon monoxide) [6]. Here, we present the first report in full detail of this photochemical carbonylation of alkyl iodides. On the basis of studies on kinetics and ESR, we could deduce that the present photochemical carbonylation proceeds via a non-chain radical mechanism. Secondly, we succeeded in developing the efficient and extremely mild carbonylation of alkyl iodides by electrolysis with $Mn_2(CO)_{10}$-K_2CO_3 catalyst system, and finally, we found that the active catalyst species in manganese-catalyzed carbonylation reaction are anionic manganese carbonyl complexes (pentacarbonylmanganates). In employment of pentacarbonylmanganates as a catalyst, thermal carbonylation of alkyl iodides proceeded efficiently at room temperature un-

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der 1 atm of carbon monoxide to give the corresponding esters in high yields without photo-irradiation and electrolysis.

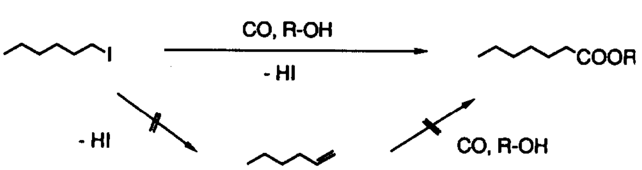
2. Results and discussion

2.1. Photochemical carbonylation of alkyl iodides in the presence of various Group 7 and 8–10 metal carbonyl catalysts

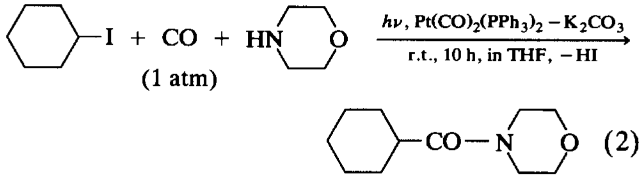
Photochemical behaviour of transition-metal carbonyls has been well studied and photogeneration of catalytically active species is of current interest in homogeneous catalysis [7]. Recently, significant progress was made on photochemical carbonylation by transition-metal complexes [8,9], but photochemical carbonylation of organic halides with transition-metal catalysts has not yet been reported. In the first place, we discovered that primary, secondary and tertiary alkyl iodides are smoothly carbonylated by the catalyst system of $Pt(CO)_2(PPh_3)_2$-K_2CO_3 under photo-irradiation (eqn. (1) and Runs 7–11 in Table 1).

$$\underset{(1\ \text{atm})}{R{-}I + CO} + R'{-}OH \xrightarrow[\text{r.t., 10–20 h, in THF, } -HI]{h\nu,\ [Pt]\text{-}K_2CO_3} R{-}COO{-}R' \quad (1)$$

Several platinum complexes such as $PtCl_2(PPh_3)_2$, $PtCl_2(P(^iPr)_3)_2$ and $PtCl_2(AsPh_3)_2$ also showed the catalytic activity (Runs 3–6), but $Pt(CO)_2(PPh_3)_2$ is the most effective catalyst precursor (Run 7). In this carbonylation, the iodide was directly replaced by the alkoxycarbonyl group, and no isomeric products were obtained (Runs 10 and 11). Unfortunately, alkyl bromides, alkyl chlorides and aryl halides such as iodobenzene were not carbonylated at all under the present reaction conditions. When 2-propanol and 2,2,2-trifluoroethanol were employed instead of methanol, the corresponding esters were also obtained in good yields (*cyclo*-$C_6H_{11}COOCH(CH_3)_2$; 87% (GLC yield), *cyclo*-$C_6H_{11}COOCH_2CF_3$; 40% (isolated yield)). When amines were employed as a nucleophile in our previous system [3], they easily formed quaternary ammonium salts with alkyl iodides and carbonylation of alkyl iodides did not occur at all. In the present reaction, however, amines could be used as a nucleophile and gave the corresponding amides in good yields (eqn. (2)).



Scheme 1.

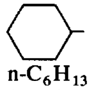
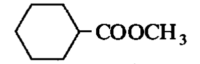


(2)

Isolated yield: 75%

In order to examine the possibility that the present carbonylation proceeds via an alkene intermediate which may be generated by dehydrohalogenation of alkyl iodide prior to its direct carbonylation, 1-hexene in place of 1-iodohexane was treated under the same

TABLE 1. Platinum complex-catalyzed photochemical carbonylation of alkyl iodides [a]

Run	Alkyl iodide	Pt complex	Conv. (%) [b]	Product	Yield (%) [c]	Light
1	n-C_6H_{13}-I	–	0	–	0	UV
2	n-C_6H_{13}-I	$PtCl_2(PPh_3)_2$	0	–	0	–
3	n-C_6H_{13}-I	$PtCl_2(PPh_3)_2$	49	n-C_6H_{13}-$COOCH_3$	15	visible
4	n-C_6H_{13}-I	$PtCl_2(PPh_3)_2$	64	n-C_6H_{13}-$COOCH_3$	41	UV
5	n-C_6H_{13}-I	$PtCl_2(P(i\text{-}Pr)_3)_2$	93	n-C_6H_{13}-$COOCH_3$	48	UV
6	n-C_6H_{13}-I	$PtCl_2(AsPh_3)_2$	92	n-C_6H_{13}-$COOCH_3$	55	UV
7	n-C_6H_{13}-I	$Pt(CO)_2(PPh_3)_2$	90	n-C_6H_{13}-$COOCH_3$	67 (52)	UV
8	n-$C_{10}H_{21}$-I	$Pt(CO)_2(PPh_3)_2$	77	n-$C_{10}H_{21}$-$COOCH_3$	76	UV
9		$Pt(CO)_2(PPh_3)_2$	87		84 (62)	UV
10	n-$C_6H_{13}CH(CH_3)$-I	$Pt(CO)_2(PPh_3)_2$	75	n-$C_6H_{13}CH(CH_3)$-$COOCH_3$	(46)	UV
11	$(CH_3)_3C$-I	$Pt(CO)_2(PPh_3)_2$	–	$(CH_3)_3C$-$COOCH_3$	63	UV

[a] A mixture of alkyl iodide (5.0 mmol), MeOH (30 mmol), Pt complex (0.25 mmol), K_2CO_3 (3.0 mmol) and THF (7.5 ml) was irradiated in a 50 ml Pyrex flask by a 200 W high pressure mercury lamp for 10 h at room temperature under 1 atm of CO (balloon). [b] Conversion of alkyl iodide determined by GLC. [c] Determined by GLC based on the amount of alkyl iodide charged; figures in parentheses are isolated yields.

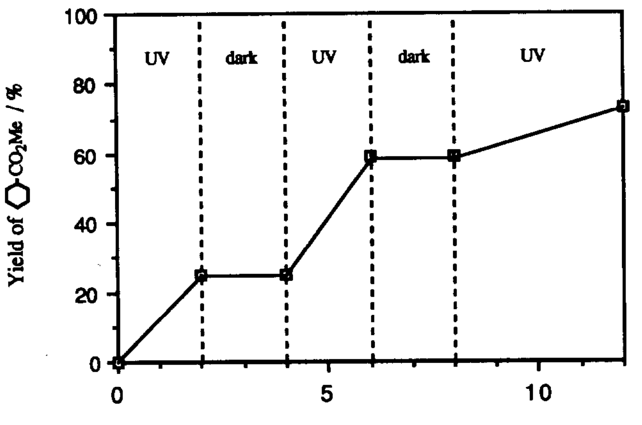
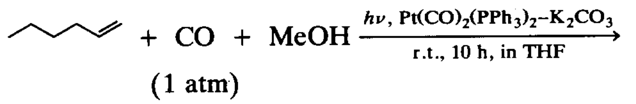


Fig. 1. Effect of photo-irradiation on $Pt(CO)_2(PPh_3)_2$-catalyzed carbonylation of iodocyclohexane.

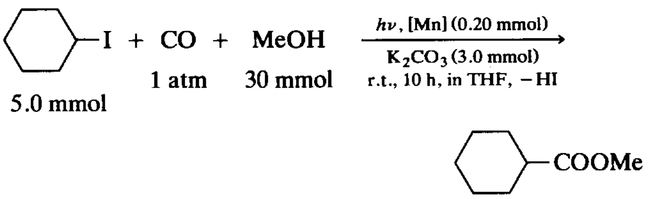
reaction conditions. However, hydroesterification of 1-hexene did not proceed at all and 1-hexene was recovered intact (eqn. (3)). Thus, the mechanism via an alkene intermediate can be excluded (Scheme 1).



no reaction (3)

Photo-irradiation is essential for the present carbonylation and no carbonylation proceeded without photo-irradiation (Run 2). With visible light-irradiation, the rate of the carbonylation was very slow and the catalytic activity was quite low (Run 3). Furthermore, as soon as the UV light was turned off, the reaction ceased completely and the carbonylation proceeded only during photo-irradiation (Fig. 1). This clearly indicates that continuous irradiation is necessary to maintain the catalytic activity.

Furthermore, to our great surprise, the various Group 7 and 8–10 metal carbonyls as well as platinum complexes effectively catalyzed the present photochemical carbonylation. The results are summarized in Table 2. Stoichiometric reactions of Group 6 and 7 metal carbonyls with organic halides [10] and their photochemistry [11] were extensively studied, but to our knowledge, catalytic carbonylation using them has not yet been reported. Although Group 6 metal carbonyls such as $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were not good catalysts for the present reaction, Group 7 metal carbonyls such as $Mn_2(CO)_{10}$, $Ph_3SnMn(CO)_5$, $KMn(CO)_5$, $LiMn(CO)_5$, $[PPN][Mn(CO)_5]$ (PPN = bis(triphenylphosphoranylidene)ammonium) (Table 2 and eqn. (4) and $Re_2(CO)_{10}$ (Table 2) showed high catalytic activity and methyl cyclohexanecarboxylate was obtained in high yields by the photochemical carbonylation of iodocyclohexane in the presence of methanol.



[Mn] = $Ph_3SnMn(CO)_5$ Yield (GLC) = 92%
$K[Mn(CO)_5]$ 96%
$Li[Mn(CO)_5]$ 98%
$[PPN][Mn(CO)_5]$ 62% (4)

TABLE 2. Catalytic activities of various Group 6, 7, and 8–10 metal carbonyl complexes in the carbonylation of iodocyclohexane [a]

Metal carbonyl	6	7	8–10				
	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe_3(CO)_{12}$ [d]	$Fe_2(CO)_9$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
Conv. (%) [b]	12	100	51	44	48	88	49
Yield (%) [c]	5	88	33	21	36	76	47
	$Mo(CO)_6$	-	$Ru_3(CO)_{12}$ [d]	$Rh_6(CO)_{16}$ [d]	$RhCl(CO)(PPh_3)_2$	$Pd_3(CO)_3(PPh_3)_4$ [d]	
Conv. (%) [b]	11	-	100	17	48	37	
Yield (%) [c]	8	-	82	7	42	25	
	$W(CO)_6$	$Re_2(CO)_{10}$	$Os_3(CO)_{12}$ [d]	$IrCl(CO)(PPh_3)_2$		$Pt(CO)_2(PPh_3)_2$	
Conv. (%) [b]	21	87	83	44		87	
Yield (%) [c]	8	77	82	42		84	

[a] A mixture of iodocyclohexane (5.0 mmol), MeOH (30 mmol), metal carbonyl (0.25 mmol), K_2CO_3 (3.0 mmol) and THF (7.5 ml) was irradiated in a 50 ml Pyrex flask by a 200 W high pressure mercury lamp for 20 h at room temperature under 1 atm of CO (balloon). [b] Conversion of iodocyclohexane determined by GLC. [c] Yield of methyl cyclohexanecarboxylate determined by GLC based on the amount of iodocyclohexane charged. [d] Metal carbonyl (0.10 mmol) was used.

As for Group 8–10 metal carbonyls, $Co_2(CO)_8$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ showed high catalytic activity. Material balance was always high, indicating that no side reaction such as dehydrohalogenation occurred.

2.2. Mechanistic study

There has been considerable interest in the mechanisms of oxidative addition of alkyl halides to transition-metal complexes [12]. Three mechanisms have been established (eqns. (5)–(7)). The first involves S_N2 displacement of the halide by a metal nucleophile, the second involves a free radical chain reaction, and the third involves a non-chain radical mechanism. In our photochemical carbonylation, oxidative addition of alkyl iodides to an active metal centre is a key step to elucidate the mechanism and we investigated the reaction concerned with platinum catalyst by kinetics and ESR spin radical trapping.

$$\mathrm{LnM + RX \longrightarrow [LnMR]^+X^- \longrightarrow LnMXR} \tag{5}$$

$$\mathrm{LnM + R^\bullet \longrightarrow [LnMR]^\bullet \xrightarrow{RX} LnMXR + R^\bullet} \tag{6}$$

$$\mathrm{LnM + RX \longrightarrow [LnM]^{+\bullet}[RX]^{-\bullet} \longrightarrow [LnMX]^\bullet + R^\bullet \longrightarrow LnMXR} \tag{7}$$

2.2.1. Kinetics

The kinetic features of the photochemical carbonylation were investigated with primary, secondary, and tertiary alkyl iodides in the presence of an excess amount of methanol and a catalytic amount of $Pt(CO)_2(PPh_3)_2$. Plots of the $-\ln(1-x/a_0)$ value, where x is the amount of generated ester and a_0 is the initial amount of alkyl iodide charged, *vs.* time show a linear relationship in all alkyl iodides. This result indicates that the reaction is of first-order dependence on the alkyl iodide concentration, since the amount of methanol was in large excess and kept constant during the reaction. When the photochemical carbonylation was carried out with different initial catalyst concentration, a straight line was obtained on plotting $\ln k_{\mathrm{obsd}}$ against $\ln[\mathrm{Pt}]_0$ and its slope was 0.23. Thus, the rate law of the present photochemical carbonylation is expressed by eqn. (8).

$$\mathrm{rate} = k_{\mathrm{obsd}}[\mathrm{R-I}]^1 = k'_{\mathrm{obsd}}[\mathrm{Pt}]_0^{0.23}[\mathrm{R-I}]^1 \tag{8}$$

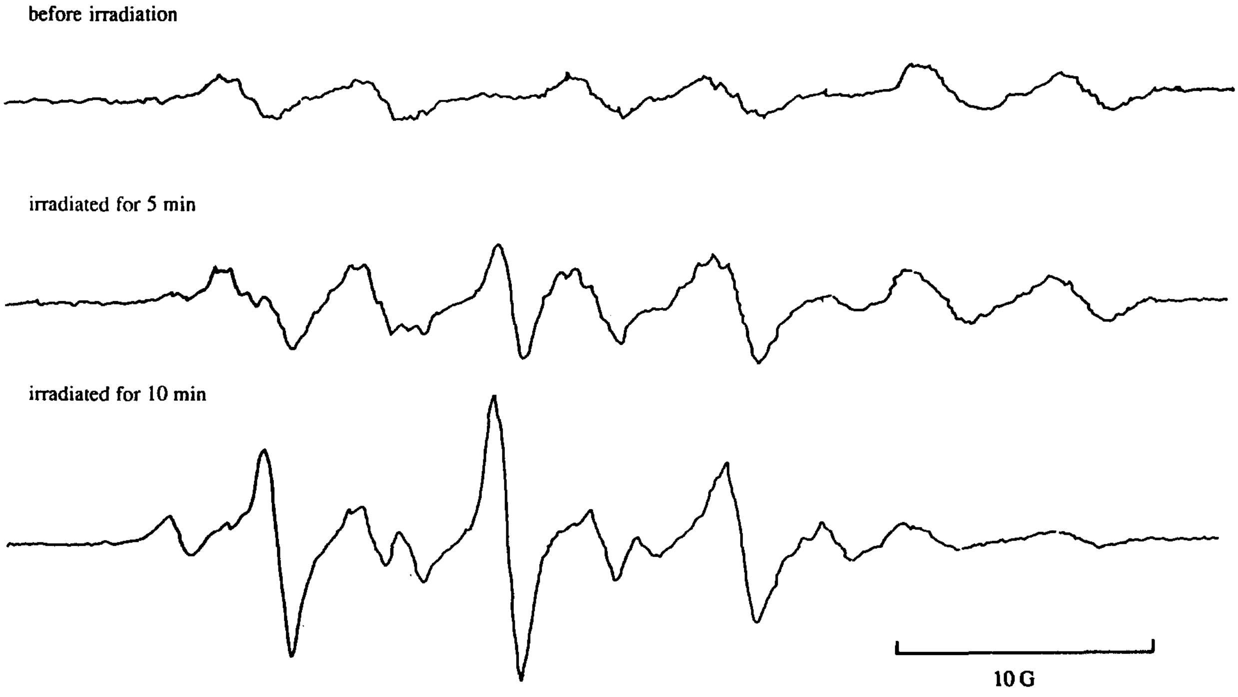
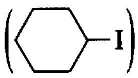


Fig. 2. ESR spectrum of iodocyclohexane-$Pt(CO)_2(PPh_3)_2$-K_2CO_3/MeOH-THF system at −50°C using nitrosodurene as a spin trapper. Irradiation: 500 W high pressure mercury lamp using Pyrex filter.

k_{obsd}: 1.83×10^{-3} (n-C_6H_{13}–I) $< 2.61 \times 10^{-3}$ (^{t}Bu–I) $< 4.77 \times 10^{-3}$ () min^{-1}

The order of k_{obsd} values was $k_{pri} < k_{tert} < k_{sec}$. Specifically, the photochemical carbonylation of primary alkyl iodides was slow compared with secondary and tertiary alkyl iodides and the present reaction involves a radical mechanism [13], not an S_N2 displacement mechanism [14]. However, addition of 2,6-di-tert-butylphenol, as a radical scavenger, did not affect the reaction (conversion of *cyclo*-$C_6H_{11}I$: 75%; yield of *cyclo*-$C_6H_{11}COOMe$: 68%), indicating that the present photochemical carbonylation did not involve a free radical chain mechanism.

2.2.2. *ESR spin radical trapping*

From the results of kinetics and effect of radical scavenger, we speculate a non-chain radical mechanism for oxidative addition of alkyl iodide to the Pt^0 centre. For further study, we employed the method of ESR spin radical trapping, whereby a reactive free radical $R^\bullet$ was trapped by a nitroso compound, R'NO, and identified by an ESR spectrum as the resultant stable nitroxyl radical, R(R')NO [15]. Figure 2 shows the ESR spectra during the photochemical carbonylation using 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene) as a spin trapper. Before irradiation, only cyclohexyl radical ($g = 2.0058$, $a_N = 13.67$ G, $a_H = 5.50$ G) was observed in the presence of the Pt^0 complex and electron transfer to alkyl iodides actually proceeded, since in the absence of Pt^0 complex, the cyclohexyl radical was not trapped. During the irradiation, a new radical species ($g = 2.0094$) was observed, which had no proton at the atom trapped by nitroxyl group of nitrosodurene and showed no satellite peak derived from platinum metal while the intensity of cyclohexyl radical was constant. At the moment, we cannot fully characterize this radical, but believe that it is an acyl radical generated from the reaction of iodocyclohexane with $Pt(CO)_2(PPh_3)_2$.

According to the studies of photochemical behaviour of d^8 square planar complexes and various transition-metal carbonyls, almost all intermediates and observed transients are formed via initial photo-dissociation of carbon monoxide ligand [16]. Indeed, when $Os_3(CO)_{12}$ was used in the present reaction, the formation of the recently reported $Os_3(CO)_{11}$ [17] was confirmed by FT-IR absorption bands at 2097, 2066, 2027 and 1996 cm^{-1}. Consequently, these results suggest that in the present reaction, photochemical dissociation of carbon monoxide from metal carbonyls would first generate a coordinatively unsaturated active catalyst species and subsequently, oxidative addition of alkyl iodide occurs to give σ-alkyl metal species. If the general migratory insertion of carbon monoxide into alkyl-metal bond proceeds, this insertion reaction must compete with β-hydride elimination reaction and the yields of the generated esters should be quite low. In consideration of the high efficiency of the present carbonylation and the results of kinetics and ESR studies, we should consider the radical mechanism for the present carbonylation. Namely, the homolytic bond cleavage of the σ-alkyl–metal bond would occur to give a tightly caged alkyl radical (not a free radical) which can be carbonylated by an assistance of the metal. Continuous photo-irradiation might be necessary for maintaining the constant homolytic bond cleavage and the generation of alkyl radicals [18*].

2.3. *Manganese-catalyzed electrochemical and thermal carbonylation of alkyl iodides*

The use of electrochemistry for organic and organometallic synthesis is well established [19] and electro-reductive removal of halogen atom of organic halides has been intensively investigated, particularly from a mechanistic viewpoint [20]. However, electrochemical transformations of organic halides have been limited to reduction [21], coupling [22] and allylation of carbonyl compounds [23]. Recently, electrochemical carbonylations of alkyl halides using a stoichiometric amount of $Fe(CO)_5$ have been reported [24] but the catalytic carbonylation of alkyl halides by electrolysis using transition-metal complexes has not yet been reported. As mentioned above, we succeeded in developing the photochemical carbonylation of alkyl iodides having β-hydrogens on sp^3-carbons using various Groups 7 and 8–10 metal carbonyl catalysts. If the electron transfer is a key step in the carbonylation of alkyl iodides, there exists a possibility that the carbonylation could also be accomplished by electrolysis. In fact, we developed the first manganese-catalyzed electrochemical carbonylation of alkyl iodides under extremely mild reaction conditions (eqn. (9)).

$$\underset{(1\ \text{atm})}{R{-}I + CO} + R'{-}OH \xrightarrow[\text{r.t., 10–24 h, in THF, } -\text{HI}]{+\text{e, [Mn]-}K_2CO_3 \\ \hline Et_4NOTs} R{-}COO{-}R' \quad (9)$$

Results are summarized in Table 3. Unlike photochemical carbonylation, only $Mn_2(CO)_{10}$ showed high catalytic activity (Run 1). Other manganese complexes such as $MeCpMn(CO)_3$, $Mn(OAc)_2 \cdot 4H_2O$, $Mn(acac)_3$ and other transition-metal complexes such as Pt-$(CO)_2(PPh_3)_2$ and $Ru_3(CO)_{12}$, which showed high catalytic activity in photochemical carbonylation, showed no cat-

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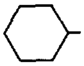
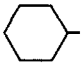
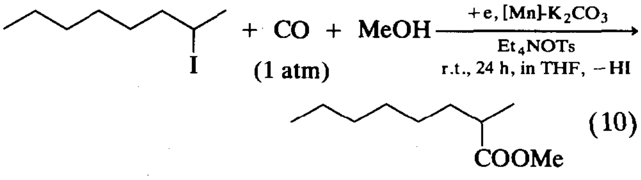
* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Electrochemical carbonylation of iodocyclohexane: Catalytic activity of several transition-metal complexes [a]

Run	Catalyst (mmol)	Conv. of -I (%) [b]	Yield of -COOMe (%) [b]
1	$Mn_2(CO)_{10}$ (0.50)	83	60 (55) [c]
2	$MeCpMn(CO)_3$ (1.0)	42	0
3	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	31	2
4	$Mn(acac)_3$ (1.0)	66	4
5	$Pt(CO)_2(PPh_3)_2$ (0.50)	66	5
6	$Ru_3(CO)_{12}$ (0.20)	39	6

[a] A mixture of iodocyclohexane (5.0 mmol), MeOH (5.0 ml), catalyst (0.20–1.0 mmol), K_2CO_3 (3.0 mmol), Et_4NOTs (0.50 g) and THF (15 ml) was electrolyzed with regulated DC power (5.0 mA/cm^2) for 24 h at room temperature under 1 atm of CO (balloon). [b] Determined by GLC. [c] Figure in parentheses is isolated yield.

alytic activity (Runs 2–6). Several alkyl iodides other than iodocyclohexane were also carbonylated by this system (eqns. (10), (11)). Under an argon atmosphere, neither carbonylation of iodocyclohexane nor decomposition of $Mn_2(CO)_{10}$ proceeded.



(10)

Isolated yield: 76%

$$n\text{-}C_6H_{13}\text{-}I + CO + MeOH \xrightarrow[\text{r.t., 10 h, in THF, } -HI]{+e,\ [Mn]\text{-}K_2CO_3,\ Et_4NOTs} n\text{-}C_6H_{13}\text{-}COOMe \quad (11)$$

(1 atm)

Isolated yield: 20%

Figure 3 shows the ESR spectrum of the present reaction system before electrolysis using nitrosodurene as a spin radical trapper. When $Mn_2(CO)_{10}$ was charged in the system, $^\bullet Mn(CO)_5$ radical was readily formed together with the generation of cyclohexyl radical. Thus, electrolysis was not essential for the generation of both $^\bullet Mn(CO)_5$ radical and cyclohexyl radical, and there exist two possibilities for the role of electrolysis [25*]. In the present reaction, Mn^{II} species would be generated from the general oxidative addition of alkyl iodides to an active Mn^0 species and finally converted into $H\text{-}Mn^{II}\text{-}I$ after the nucleophilic attack of alcohol to an acy–Mn^{II}–I intermediate. One possibility of the

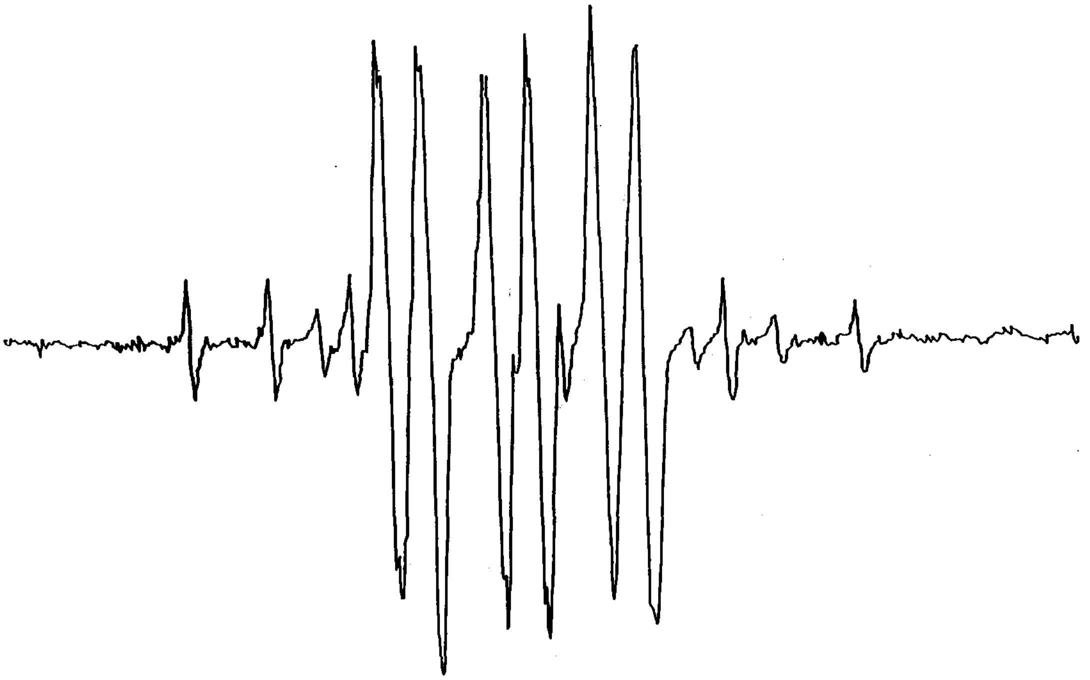


Fig. 3. ESR spectrum of iodocyclohexane-$Mn_2(CO)_{10}$-K_2CO_3/MeOH-THF system at −50°C using nitrosodurene as a spin trapper.

role of electrolysis was cathodic electroreduction of such Mn^{II} species to catalytically active Mn^0 species [22a,d]. However, in the absence of K_2CO_3, electrochemical carbonylation did not occur at all and we consider that the regeneration of Mn^0 from Mn^{II} was performed by base-assisted elimination of HI.

Another possibility is that electroreduction of $\cdot Mn(CO)_5$ radical generated $Mn(CO)_5^-$ *in situ*. Indeed, manganese carbonyl species which showed the FT-IR absorption bands at 2048, 2041, 1997, 1971 and 1931 cm^{-1} were detected after electrochemical carbonylation for 24 h. These species are considered to be a mixture of $Mn(CO)_5I$ [26] and an anionic manganese carbonyl species, $Mn(CO)_5^-$ [27].

Substitution reactions of alkyl halides, RX, with carbonyl metallates, $M(CO)_n^-$ ($Mn(CO)_5^-$, $Co(CO)_4^-$ *etc.*), in homogeneous solutions play key roles in catalytic and stoichiometric carbonylation of RX [28,29]. For example, it is well established that the reaction of alkyl iodides such as methyl iodide with $Mn(CO)_5^-$ gives $CH_3Mn(CO)_5^-$ [30] and subsequent carbonylation of $CH_3Mn(CO)_5$ including its stereochemistry is also well studied [31]. Although the generally high stereoselectivity of these reactions has been widely interpreted as evidence against the intermediacy of free alkyl radicals and in favour of an S_N2 pathway, radical pathways initiated by single electron transfer (SET) are also possible in many cases (eqn. (12)) [32,33].

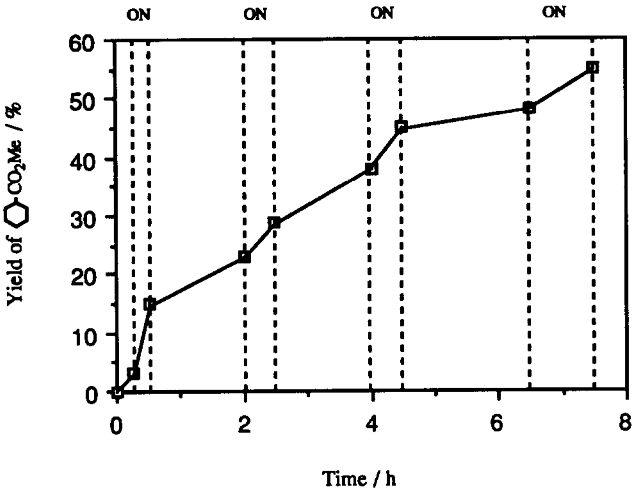
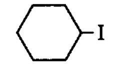
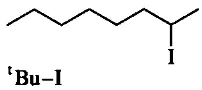
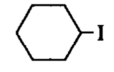


Fig. 4. Effect of electrolysis on $Mn_2(CO)_{10}$-catalyzed carbonylation of iodocyclohexane.

$$\begin{array}{l} R\text{-}X + M(CO)_n^- \xrightarrow{SET} [R\text{-}X^{-\bullet}, {}^\bullet M(CO)_n] \xrightarrow{-X^-} \\ \qquad [R^\bullet\ {}^\bullet M(CO)_n] \longrightarrow RM(CO)_n \\ \qquad\quad \Downarrow \\ \left(R^\bullet + {}^\bullet M(CO)_n \longrightarrow R\text{-}R + M_2(CO)_{2n} \right) \end{array} \qquad (12)$$

TABLE 4. Pentacarbonylmanganate-catalyzed carbonylation of alkyl iodides [a]

$$R\text{-}I + CO + MeOH \xrightarrow[\text{in THF, r.t., } -HI]{[Mn]\text{-}K_2CO_3} R\text{-}COOMe$$

Run	R-I	Catalyst (mmol)	Time (h)	Conv. of alkyl iodide (%) [b]	Yield of ester (%) [b]
1		$Mn_2(CO)_{10}$ (0.05)	6	28	22
2		$Ph_3SnMn(CO)_5$ (0.20)	6	21	18
3		[PPN][$Mn(CO)_5$] (0.20)	6	27	23
4		$KMn(CO)_5$ (0.10)	6	64	62
5		$KMn(CO)_5$ (0.10)	6	55	37
6	^tBu-I	$KMn(CO)_5$ (0.10)	6	83	35
7		$LiMn(CO)_5$ (0.20)	24	86	68
8		$KMn(CO)_5$ (0.20)	24	83	73
9		$NaMn(CO)_5$ (0.20)	24	100	84
10 [c]		$KMn(CO)_5$ (0.10)	6	48	37
11 [d]		$KMn(CO)_5$ (0.10)	6	0	0

[a] A mixture of iodocyclohexane (5.0 mmol), MeOH (30 mmol), catalyst, K_2CO_3 (3.0 mmol) and THF (7.5 ml) was stirred at room temperature under 1 atm of CO (balloon).

[b] Determined by GLC based on the amount of alkyl iodide charged.

[c] 2,6-Di-tert-butylphenol (1.0 mmol) was added.

[d] Galvinoxyl (1.0 mmol) was added.

In the present manganese-catalyzed electrochemical carbonylation, the ESR detection of $^{\bullet}Mn(CO)_5$ radical [34] and cyclohexyl radical ($g = 2.0058$, $a_N = 13.67$ G, $a_H = 5.50$ G) and the formation of halometal carbonyls all support a radical mechanism, but the finding that homocoupling of cyclohexyl radical to form bicyclo-

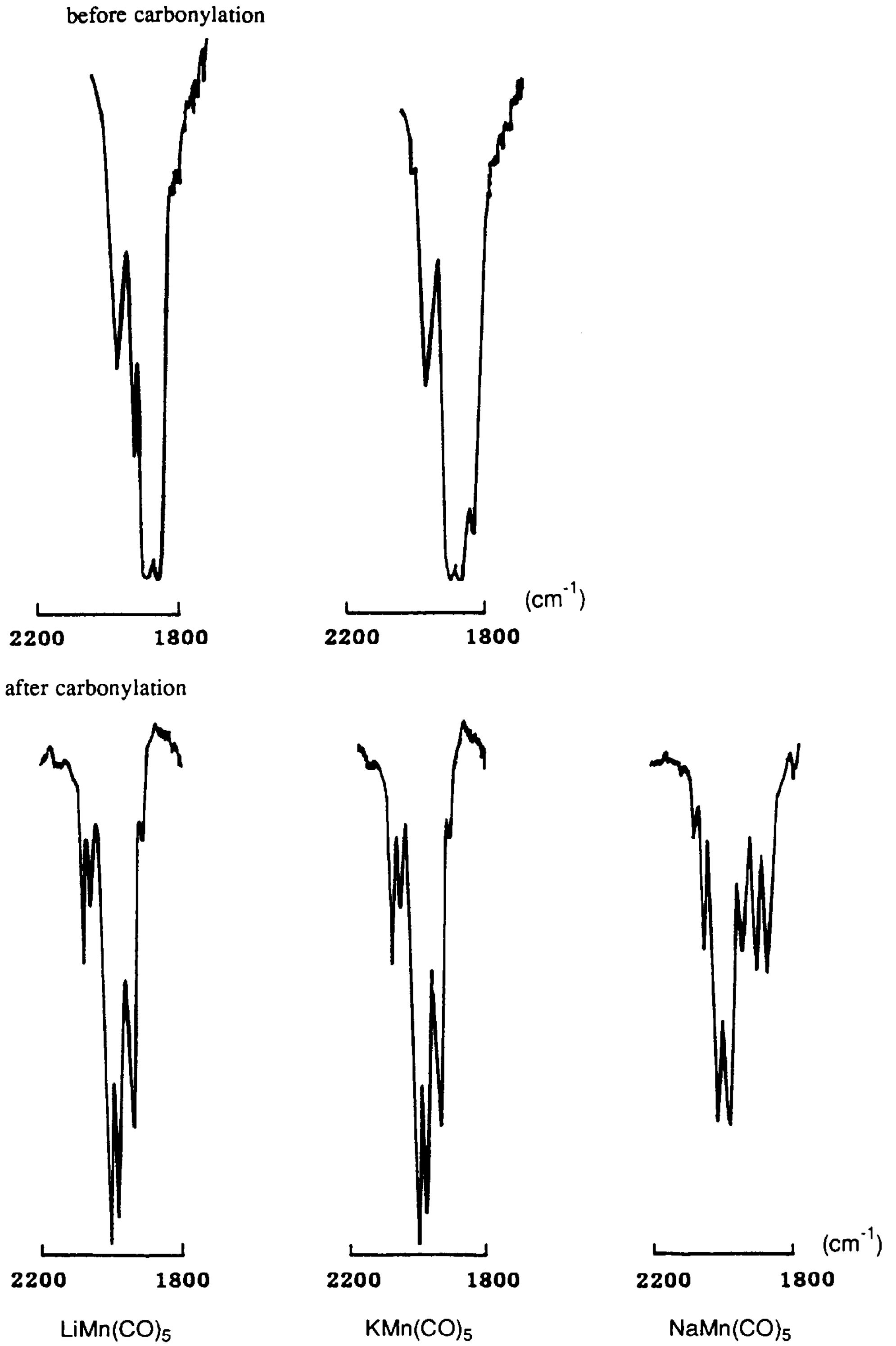
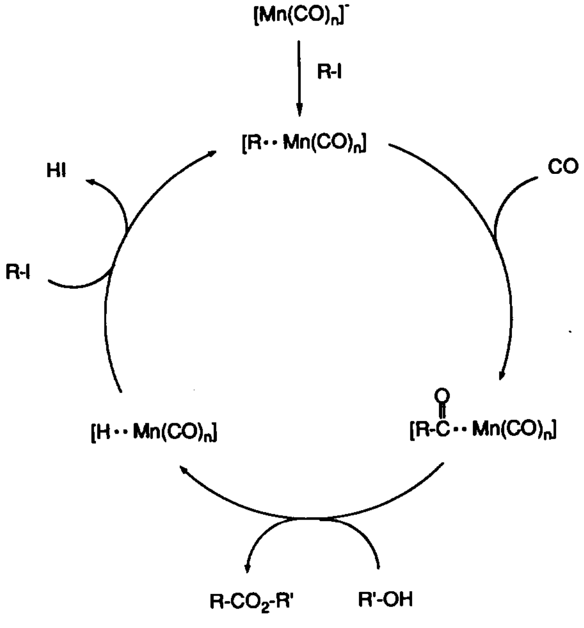


Fig. 5. FT-IR spectrum of pentacarbonylmanganates before and after carbonylation of iodocyclohexane.

hexyl did not proceed at all strongly suggests that the radical species involved in the present reaction is not free, but tightly caged. Namely, the similar homolytic bond cleavage in σ-alkyl manganese species as that in the photochemical carbonylation occurs to give alkyl radical that is bound by the metal. In contrast to the photochemical carbonylation, once the carbonylation reaction started, the reaction did not cease completely when the electrolysis was terminated (Fig. 4). This result can be rationalized by consideration of the facility of the homolytic bond cleavage of σ-alkyl–Mn bond [34].

Consequently, the electrolysis is considered to be required only for the generation of $Mn(CO)_5^-$ from $^{\bullet}Mn(CO)_5$. In fact, when $Mn(CO)_5^-$ which was separately prepared from $Mn_2(CO)_{10}$ [27] was employed as a catalyst, the thermal carbonylation of alkyl iodides smoothly proceeded at room temperature under 1 atm of carbon monoxide without photo-irradiation and electrolysis to give the corresponding esters in good yields. The results are summarized in Table 4. Several pentacarbonylmanganates such as $LiMn(CO)_5$, $KMn(CO)_5$ and $NaMn(CO)_5$ showed high catalytic activity (Runs 4–9), whereas the neutral $Mn_2(CO)_{10}$ and $Ph_3SnMn(CO)_5$ complexes and stable manganate salt such as $[PPN][Mn(CO)_5]$ only assisted the stoichiometric carbonylation of iodocyclohexane (Runs 1–3). In the present reaction, the effect of radical scavenger appeared clearer than that in the photochemical carbonylation. For example, when galvinoxyl was added as a radical scavenger, the carbonylation completely ceased (Run 11). This result suggests that the binding effect of the alkyl radical by the metal would be weaker than that in the photochemical carbonylation, because of the facility of homolytic bond cleavage of the σ-alkyl–Mn bond (*vide supra*). After the carbonylation, all of the reaction solutions using $LiMn(CO)_5$, $KMn(CO)_5$ and $NaMn(CO)_5$ showed the same FT-IR absorption bands of their carbonyl ligands (Fig. 5). The results are consistent with the above mentioned absorption bands of electrochemical carbonylation using $Mn_2(CO)_{10}$ catalyst. Thus, the same active catalyst species is formed in both electrochemical carbonylation using $Mn_2(CO)_{10}$ and thermal carbonylation using pentacarbonylmanganates.



Scheme 2.

Finally, the most plausible catalytic cycle of the present manganese-catalyzed carbonylation of alkyl iodides is illustrated in Scheme 2.

In conclusion, we have succeeded in developing a new method for effective carbonylation of alkyl iodides in the presence of various Group 7 and 8–10 metal carbonyl catalysts by photo-irradiation. Further, electrochemical and thermal carbonylations of alkyl iodides by manganese carbonyl complexes under extremely mild reaction conditions were explored. These carbonylation reactions all proceed via a non-chain radical mechanism.

3. Experimental details

3.1. Materials

The reagents employed in this study were dried and purified by the usual procedures. Carbon monoxide (> 99.9%) was used without further purification. $PtCl_2(PPh_3)_2$ [35], $PtCl_2(P(^iPr)_3)_2$ [36], $PtCl_2(AsPh_3)_2$ [37], $Pt(CO)_2(PPh_3)_2$ [38], $RhCl(CO)(PPh_3)_2$ [39] and $Pd_3(CO)_3(PPh_3)_4$ [40] were prepared by the literature methods. Other Group 6, 7 and 8–10 carbonyl complexes were purchased from Strem Chemicals and $Mn(OAc)_2 \cdot 4H_2O$ and $Mn(acac)_3$ were purchased from Tokyo Kasei Kogyo. They were used without further purification. $LiMn(CO)_5$, $KMn(CO)_5$, $NaMn(CO)_5$, $Ph_3SnMn(CO)_5$ and $[PPN][Mn(CO)_5]$ were prepared by the literature method [27]. Et_4NOTs was purchased from Aldrich Chemical Company and dried under high vacuum before use. 2-Iodooctane was prepared by the literature method from 2-octanol [41].

3.2. General procedure

3.2.1. Photochemical carbonylation

A mixture of alkyl iodide (5.0 mmol), alcohol (30 mmol), catalyst (0.10–0.25 mmol), K_2CO_3 (3.0 mmol) and THF (7.5 ml) was placed in a 50 ml Pyrex flask and irradiated by a 200 W high pressure mercury lamp for 10–20 h at room temperature under 1 atm of carbon monoxide (balloon). The resulting light yellow solution was analyzed by GLC and FT-IR.

3.2.2. Electrochemical carbonylation

Electrolysis was carried out in a normal undivided cell fitted with two platinum plate electrodes (2 × 2 cm^2). A mixture of alkyl iodide (5.0 mmol), $Mn_2(CO)_{10}$ (0.50 mmol), K_2CO_3 (3.0 mmol), Et_4NOTs (0.50 g), alcohol (5.0 ml) and THF (15 ml) was charged into a cell and after purging with carbon monoxide, regulated DC power (5 mA/cm^2) was supplied for 10–24 h at room temperature under 1 atm of carbon monoxide (balloon). The resulting yellow-brown solution was analyzed by GLC and FT-IR.

3.2.3. Thermal carbonylation

A mixture of alkyl iodide (5.0 mmol), alcohol (30 mmol), pentacarbonylmanganate (0.10–0.20 mmol), K_2CO_3 (3.0 mmol) and THF (7.5 ml) was placed in a 50 ml Pyrex flask and stirred for 6–24 h at room temperature under 1 atm of carbon monoxide (balloon). The resulting yellow-brown solution was analyzed by GLC and FT-IR.

3.3. Analytical procedure

The product was isolated by careful vacuum distillation and/or medium pressure column chromatography (absorbent: silica gel or aluminium oxide; eluent: a mixture of hexane and ethyl acetate). The identification of all products was carried out by ^1H NMR, ^{13}C NMR, FT-IR spectroscopy and GC-MS.

GLC analyses were performed on Shimadzu GC-4CM and GC-8A chromatographs equipped with columns (3 mm i.d. × 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 Uniport HP, 60-80 mesh). IR spectra were measured on a Nicolet 5MX Fourier transform infrared spectrophotometer. ^1H NMR spectra were obtained at 90 MHz with a JEOL JNM FX-90Q spectrometer and ^{13}C NMR spectra were recorded at 25.05 MHz with a JEOL JNM FX-100 spectrometer. Samples were dissolved in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. Mass spectra (MS) were obtained on a Shimadzu QP-1000 spectrometer. ESR spectra were obtained on a JEOL PE-2X spectrometer.

The analytical data of all products were consistent with those of the authentic samples and/or separately prepared samples from the corresponding carboxylic acids and alcohols or amines.

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