bond stretches 0.26 Å, the OH distance is 1.16 Å, and the H_2CH angles are 97.0° at the transition state, again similar to CH_4. The OHC angle is nearly 180°, and the tilt of the CH axis from the surface normal is nearly 40°. The O atoms each move 0.38 Å in the (001) direction. The MO correlation diagram is shown in Figure 8. Even before the CH bond is stretched, its proximity causes the surface p_z and p_x orbitals to hybridize: one hybrid is rotated to form the three-centered CHO donation bond and the other one is perpendicular to it and nonbonding with CH as shown in the left-hand column of Figure 8. Otherwise, the correlation diagram is essentially the same as for methane CH activation (Figure 3). At the transition state the antibonding counterpart to the σ-donation orbital has risen just past the Fermi level and has transferred an electron to the silver. By either desorbing as isobutylene or by forming isobutylene oxide (both are seen experimentally in ref 5), the radical orbital above the Ag Fermi level can be stabilized, picking up an electron to form a CC π- or CO σ-bonding orbital.

Conclusions

While not as active as O⁻ on oxide surfaces, oxygen atoms (formally O²⁻) on a silver surface are clearly able to abstract hydrogen atoms from methyl groups. Empty metal surface orbitals at the Fermi level accept the electron that is released when O²⁻ becomes OH⁻. It is expected that this reaction can occur on other metal surfaces with oxygen atoms chemisorbed on them. The activation energy should decrease for metals with higher electronegativities. The insertion of O(ads) into a methane CH bond to form CH_3OH(ads) is predicted to be possible in our calculations. In this case two electrons are promoted to the metal. It would be interesting to look for this potential carbene-like oxygen insertion reactivity over metal surfaces with oxygen overlayers.

Carbonylation of Hydrocarbons via C–H Activation Catalyzed by RhCl(CO)(PMe₃)₂ under Irradiation

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Abstract: C–H bonds in hydrocarbons are carbonylated into aldehydes by reaction with carbon monoxide in the presence of RhCl(CO)(PR₃)₂ under irradiation. The reaction proceeds at an ambient temperature under an atmospheric pressure of CO. The catalytic activity of RhCl(CO)(PR₃)₂ decreases in the order PMe₃ ≈ 1,3,4-trimethylphospholane ≈ 1,3,4-trimethylphospholene > P(CH₂O)₃CMe > PEt₃ ≈ PBu₃ > P(*i*-Pr)₃ ≈ PPh₃ ≈ P(OMe)₃ > dppe. The thiocyanato complex exhibits a similar catalytic activity to the chloro complex. The use of other complexes of Co, Ir, and Ru resulted in much lower catalytic activities. In the carbonylation of benzene, benzophenone and benzyl alcohol are formed as byproducts. The yield of benzaldehyde reached 3.3% on the basis of benzene. Monosubstituted benzenes are converted mainly to meta-substituted benzaldehydes. In the reaction of *n*-alkanes, a terminal methyl group is selectively carbonylated to give a linear aldehyde. These regioselectivities are explainable in terms of thermodynamic stability of hydridoalkyl (or alkyl) intermediates. The linear aldehyde obtained from *n*-alkane undergoes a secondary photoreaction (Norrish Type II) to afford a terminal olefin and acetaldehyde. The catalytic activity, regioselectivity of the carbonylation, and the occurrence of Norrish Type II reaction are markedly affected by irradiation wavelength. RhCl(PMe₃)₂ formed via CO dissociation is proposed as a possible active species for the C–H activation.

Selective functionalization of hydrocarbons through C–H bond activation has been one of the most challenging problems facing organic chemists. Since some enzymes in nature are good catalysts for a wide range of transformations of alkanes, growing efforts have been made to synthesize artificial systems capable of C–H bond activation, in particular at the terminal methyl group. There are two different approaches to attain C–H bond activation. One is to mimic the structure of the active site of enzymes. So called "P-450 model systems" are examples of such approaches. However, the regioselectivity so far achieved has been poor even though sophisticated model systems like bulky porphyrins[1] have been devised. The other approach is to mimic only the function of enzymes by designing artificial reaction systems where the transformation mechanism may be completely different from enzymatic processes. A recent interesting example along this line is the zeolite-supported heterogeneous catalyst with which terminal selective oxidation of *n*-alkane was attempted.[2] However, the regioselectivity was also unsatisfactory. Another possibility belonging to the latter approach might be the renewed interest in the oxidative addition of alkane C–H bonds initiated by Bergman, Graham, and Jones.[3] In their systems, the primary C–H bond of terminal methyl groups was selectively cleaved while secondary C–H bonds remained intact.[3c,d] This selectivity is the reverse of that achieved by conventional functionalizations of alkanes with radicals or strong acids[4] and is not explainable by the order of bond strength. We have been investigating the application of this unique elemental step (oxidative addition of C–H bonds) to catalytic reactions, resulting in the recent development of the

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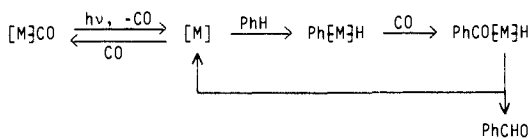[‡] Mitsubishi Kasei Corporation.

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[M₃CO] $\underset{CO}{\overset{h\nu, -CO}{\rightleftharpoons}}$ [M] $\xrightarrow{PhH}$ Ph[M]H $\xrightarrow{CO}$ PhCO[M]H

PhCHO

Figure 1. Carbonylation of benzene via C–H activation.

RhCl(CO)(PMe₃)₂-*hν* system. This system catalyzes various types of C–H bond functionalization such as carbonylation, isonitrile insertion, C=C double bond insertion, C≡C triple bond insertion, dehydrogenation, dehydrogenative coupling, etc.[5] We wish to disclose here the details of the new carbonylation procedure,[5b–f] including the first successful example of terminal selective catalytic functionalization of alkanes without using the enzymatic system.[6]

Although the carbonylation of methane in the presence of Cp₂TiCl₂ and AlEt₃ has been reported under very high pressure,[7] the reaction is not catalytic. On the other hand, the photoassisted carbonylation of benzene to give benzaldehyde has also been reported by Eisenberg et al.[8] However, the performance of their systems was unsatisfactory; the highest turnover and the highest PhCHO concentration were only 2 and 15 mM, respectively. Moreover, they have claimed a quite pessimistic view of improving the aldehyde yield, saying that the low yield they obtained is not due to kinetic inactivity of the system but to thermodynamic equilibration between carbonylation and decarbonylation (eq 1).

$$PhH + CO \rightleftharpoons PhCHO \qquad (1)$$
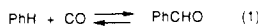
In reality, however, our catalyst RhCl(CO)(PMe₃)₂ is much more effective. For example, its turnover rate for benzene carbonylation is 30 to 40 times higher than that of RhCl(CO)(PPh₃)₂, which is the most active catalyst reported by Eisenberg; the maximum PhCHO concentration reached 370 mM.

Results and Discussions

Catalyst Effect. In order to undergo C–H oxidative addition, the complex should be coordinatively unsaturated. Irradiation has been known to be an effective way to dissociate ligands such as carbonyl, phosphine, and dihydrogen.[9] Hence, we planned the photoassisted carbonylation of C–H bonds via the catalytic

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Table I. Effect of Phosphine on the Carbonylation of Benzene by RhCl(CO)(PR₃)₂[a]

phosphine	IR absorption of CO,[b] cm⁻¹	Rh concn, mM	yield of PhCHO,[c] %/Rh
PMe₃	1970	7	1540 (147)
PBu₃	1955	7	398 (6)
PEt₃	1957	7	328 (4)
P(i-Pr)₃	1947	7	34
P(p-tolyl)₃	1979	7	63
PPh₃	1982	7	39
P(OMe)₃	2011	7	37
PMe₃	1970	0.7	6520 (738)
⟨PMe⟩	1954	0.7	6390 (780)
⟨PMe⟩	1963	0.7	6850 (937)
P(CH₂O)₃CMe	2000	0.7	3330 (732)
PBu₃	1955	0.7	1850 (197)
PEt₃	1957	0.7	1340 (88)
PPh₃	1982	0.7	213 (4)
dmpm[d]	1962[e]	0.7	16 (9)
dppe[f]	2018	0.7	6

[a] Rh 0.21 mmol (7 mM) or 0.021 mmol (0.7 mM) in 30 mL of benzene, CO 1 atm, room temperature, 16.5 h, irradiated through Pyrex (>290 nm). [b] CHCl₃ solution. [c] The figures in parentheses are the yields of PhCH₂OH. [d] Bis(dimethylphosphino)methane. The complex is dimeric (see Experimental Section). [e] Nujol mull. [f] 1,2-Bis(diphenylphosphino)ethane.

Table II. H/D Exchange of the PMe₃ Ligand in the Carbonylation of Benzene-*d₆* by the RhCl(CO)(PMe₃)₂-*hν* System[a]

time, h	RhCl(CO)(PMe₃)₂-*dₙ*, %				
	d₀	*d₁*	*d₂*	*d₃*	*d₄*
0	100	0	0	0	0
3	67	28	5	0	0
9	40	40	17	3	1
15	26	34	27	12	1

[a] Rh 0.021 mmol, C₆D₆ 30 mL, CO 1 atm, room temperature, irradiated through Pyrex (>290 nm).

cycle depicted in Figure 1, which involves photoassisted CO dissociation, oxidative addition of the C–H bond, CO insertion to the carbon–metal bond, and reductive elimination of an aldehyde. As for the central metal of the complex, we first chose rhodium since rhodium complexes had been known to be highly active for both C–H bond activation and carbonylation.

The carbonylation of benzene was carried out in the presence of typical Rh(0) and Rh(I) carbonyl complexes under irradiation with an immersion-type high-pressure mercury lamp. The preliminary experiments with Rh₄(CO)₁₂, Cp*Rh(CO)₂, [RhCl(CO)₂]₂, RhCl(CO)₂[P(p-tolyl)₃], and RhCl(CO)[P(p-tolyl)₃]₂ showed that only the Vaska-type rhodium complex of tri-*p*-tolylphosphine gave a small amount of benzaldehyde although the reaction was not catalytic (62%/Rh, Rh 7 mM, CO 1 atm, room temperature, 16.5 h). Judging from the IR spectra after the reaction, the complexes were found not to have been deteriorated by the irradiation.

(a) Effect of the Phosphine Ligand in RhCl(CO)(PR₃)₂. Since the Vaska-type rhodium complex was effective for the benzene carbonylation, we next investigated the effect of the phosphine ligand (Table I) on a working hypothesis that promotion of oxidative addition of the C–H bond would result in an improvement of reaction rate. One possible way to facilitate the oxidative addition is to increase the electron density of the central metal. In fact, the triethyl- or tributylphosphine complex exhibited about ten times higher activity than the triphenylphosphine complex. The low yields of benzaldehyde in the use of RhCl(CO)(PPh₃)₂ should be ascribed to its low catalytic activity but not to the decomposition of the complex nor the thermodynamic limitation depicted in eq 1, because the yield of benzaldehyde increased almost linearly with the reaction time in the time scale of Table I. The importance of the electron-donating ability of phosphine

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Table III. Effect of the Anionic Ligand of RhX(CO)[P(p-tolyl)$_3$]$_2$ on the Carbonylation of Benzene[a]

X	IR abs of CO.[b] cm^{-1}	PhCHO, %/Rh	decomp of PAr$_3$, %/Rh	
			ArCHO	ArPh
OH	1950	3	5	52
F	1961	19	23	41
Cl	1972	36	0	0
		(16.5 h; 249	3	2)
Br	1974	9	0	0
I	1976	6	0	0
SCN	1988	41	0	0
		(16.5 h; 193	0	0)
CN	1994	3	1	23

[a] Rh 0.021 mmol, benzene 30 mL, CO 1 atm, room temperature, 3 h, irradiated through Pyrex (>290 nm). [b] Nujol mull.

ligands is also suggested by the fact that trimethyl phosphite, which is as small as triethylphosphine, afforded very low catalytic activity. Small steric hindrance of phosphine ligand should also be important to achieve high catalytic activity; the reactivity order of trialkylphosphine complexes was PMe$_3$ > PEt$_3$ ≈ PBu$_3$ > P(i-Pr)$_3$.

The effect of phosphine stated above cannot be correlated to the UV absorption of the rhodium complexes, because the RhCl(CO)(PR$_3$)$_2$ complexes show almost the same absorption band (λ_{max} ≈ 365 nm, ϵ ≈ 4000) irrespective of phosphines.[10] Intramolecular C–H bond activation of the phosphine ligand (tail biting) as shown in eq 2 is another possible factor dictating the efficiency of intermolecular oxidative addition. Tail biting
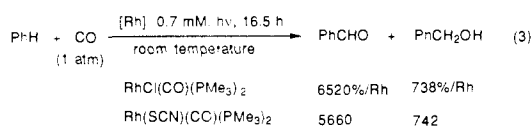
$$\text{Rh-P}\overbrace{}^{R'_2}(\text{CH}_2\text{R}) \longrightarrow \text{H-Rh}\overset{\text{HC}\overset{R}{\diagdown}}{}\text{PR}'_2 \quad (2)$$
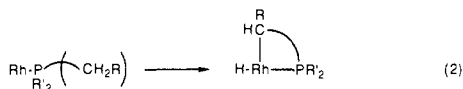
has been confirmed for various complexes through isolation of metallacyclic hydridoalkyl complexes[11] or H/D exchange on the phosphine ligands.[12] Although we also found that even RhCl(CO)(PMe$_3$)$_2$ underwent H/D exchange with benzene-d_6 under the carbonylation conditions (Table II), PMe$_3$ is likely to be much more stable against tail biting as compared with other alkylphosphines. As a matter of fact, Jones reported that Cp*Rh(PMe$_3$) did not undergo tail biting, while Cp*Rh(PMe$_2$Pr) did at the propyl group.[13] Thus, the effectiveness of PMe$_3$ shown in Table I seems reasonable also from the standpoint of depression of tail biting.

The use of a basket-type phosphine, P(CH$_2$O)$_3$CMe, which has a smaller cone angle[14] than PMe$_3$ and seems even less likely to undergo tail biting, resulted in a lower catalytic activity than the use of PMe$_3$. As judged from the ν_{CO} values (2000 and 1970 cm^{-1} for the P(CH$_2$O)$_3$CMe and PMe$_3$ complexes, respectively), this is possibly ascribed to the lower electron donating power of P-(CH$_2$O)$_3$CMe as compared with PMe$_3$. The complexes of small and basic phosphines like CH$_3$PCH$_2$CH(CH$_3$)CH(CH$_3$)CH$_2$ and CH$_3$PCH$_2$C(CH$_3$)=C(CH$_3$)CH$_2$ were as effective as the PMe$_3$ complex. The dppe complex showed quite poor catalytic performance. The dimeric complex of bis(dimethylphosphino)-methane, Cl(CO)Rh(Me$_2$PCH$_2$PMe$_2$)$_2$Rh(CO)Cl, was also a poor catalyst.

(b) Effect of the Anionic Ligand in RhX(CO)[P(p-tolyl)$_3$]$_2$. The effect of anionic ligand on the catalytic activity was examined for the tri-p-tolylphosphine complexes (Table III). Although the ν_{CO} value of the Vaska-type rhodium complexes, which is an

indicator of electron-donating ability of the anionic ligand,[15] varied widely, no clear relation was found between the catalytic activity and the ν_{CO} values. The effect is not ascribed to the change of the UV absorption of the complexes, either, because the λ_{max} value of RhX(CO)(PR$_3$)$_2$ is hardly affected by the anionic ligand.[10] Among halogeno anions, the chloro ligand gave the highest yield while either smaller (fluoro) or larger (bromo and iodo) ligands decreased the activity. The activity of the thiocyanato complex was as high as that of the chloro complex. Other anionic ligands such as cyano or hydroxo exhibited very low activity. In the reaction with the hydroxo, fluoro, or cyano complexes, p-tolualdehyde and p-methylbiphenyl were detected showing the decomposition of the phosphine ligand. However, when the anionic ligand was chloro, bromo, iodo, or thiocyanato, such phosphine decomposition products were not observed. We also synthesized the thiocyanato complex with trimethylphosphine ligand; the activity for benzene carbonylation was almost the same as that of the chloro complex (eq 3). Considering both the catalytic activity and the ease of preparation, the chloro complex seems to be the best catalyst.

$$\text{PhH} + \text{CO} \xrightarrow[\text{room temperature}]{[\text{Rh}] \quad 0.7 \text{ mM} \quad \text{hv, 16.5 h}} \text{PhCHO} + \text{PhCH}_2\text{OH} \quad (3)$$

$$\text{(1 atm)}$$

RhCl(CO)(PMe$_3$)$_2$	6520%/Rh	738%/Rh
Rh(SCN)(CO)(PMe$_3$)$_2$	5660	742

(c) Performance of Other Metal Complexes. The catalytic activity of other carbonylphosphine complexes was also examined (complex 0.7 mM in benzene (or in toluene in the use of PPh$_3$ complex), CO 1 atm, room temperature, 16.5 h). Other than rhodium complexes, IrCl(CO)(PMe$_3$)$_2$ and IrCl(CO)(PPh$_3$)$_2$ exhibited some activities; the sums of the yields of aldehyde and alcohol were 46 and 7%/Ir, respectively. Ruthenium and cobalt complexes, Ru(CO)$_3$(PPh$_3$)$_2$ and AcCo(CO)(PTt$_3$)$_2$, also exhibited low activities (10%/Ru and 1%/Co).[16] CoCl(CO)$_2$(PPh$_3$)$_2$, [Co(CO)$_3$(PEt$_3$)]$_2$, Ni(CO)$_2$(PPh$_3$)$_2$, Pt(CO)(PPh$_3$)$_3$, Pt(CO)$_2$-(PPh$_3$)$_2$, and Fe(CO)$_3$(PMe$_3$)$_2$ were totally inactive. Although the performance of the non-rhodium complexes was very low, optimization of the irradiation wavelength and of the ligand effect for each metal hopefully leads to significant improvement in the activity. In many reactions with non-rhodium complexes, by-products like aldehydes and biaryls resulting from phosphorus-carbon bond cleavage were formed. However, such phosphine decomposition was negligible in the reaction with RhCl(CO)-(PR$_3$)$_2$. Hence, it is concluded that Vaska-type rhodium complexes are superior in view of not only their catalytic activity but also the stability of the complex under the reaction conditions.

Carbonylation of Benzene. (a) Byproducts. In the carbonylation of benzene with RhCl(CO)(PMe$_3$)$_2$ used as the catalyst, some amounts of byproducts are formed other than benzaldehyde such as benzyl alcohol, benzophenone, biphenyl, and benzoic acid (eq 4). Since the respective ratios of benzyl alcohol, benzophenone,

$$\text{PhH} + \text{CO} \xrightarrow[\text{hv, room temperature}]{\text{RhCl(CO)(PMe}_3\text{)}_2 \quad 0.7 \text{ mM}}$$

	PhCHO	PhCH$_2$OH	PhCOPh	Ph-Ph	PhCO$_2$H	
3 h	1370%/Rh	8	0	75	--	(4)
6 h	2610	198	32	156	trace	
18 h	7370	1090	650	372	--	
33 h	7240	1630	1660	528	≈ 100	
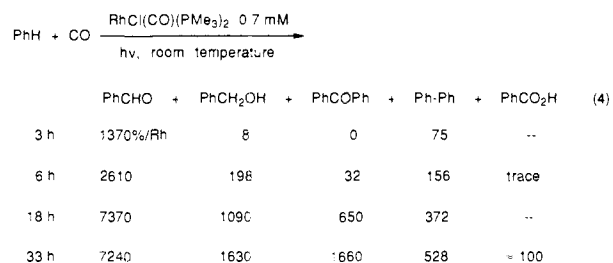
and benzoic acid to benzaldehyde clearly increased as the reaction proceeded, these compounds are presumably secondary products formed from benzaldehyde. Biphenyl seems a primary product because it is formed catalytically even under nitrogen.[5n] The hydrogen required for the formation of benzyl alcohol must have been supplied by the formation of biphenyl and benzophenone;

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Table IV. Addition of Aldehydes to the Arene Carbonylation[a]

arene (ArH)	aldehyde (RCHO)	products, turnover[b]			
		from arene		from aldehyde	
toluene	benz-aldehyde	ArCHO[c]	36	RCHO	2 (5)
		ArCH₂OH[c]	35	RCH₂OH	23 (61)
		ArAr[d]	32	RCH(OH)Ar[e]	10 (26)
		ArCOAr[c]	<7	RH	1 (2)
		ArCH(OH)Ar[c]	25		
benzene	p-tolu-aldehyde	ArCHO	47	RCHO	14 (36)
		ArCH₂OH	20	RCH₂OH	2 (5)
		ArAr	2	RCOAr	8 (20)
		ArCOAr	14	RH	1 (4)
benzene	cyclohex-anecarb-aldehyde	ArCHO	58	RCHO	1 (1)
		ArCH₂OH	35	RCH₂OH	trace
		ArAr	2	RAr	2 (5)
		ArCOAr	6	RCOAr	12 (32)
				RH	16 (43)

[a] RhCl(CO)(PMe₃)₂ 0.021 mmol, aldehyde 0.80 mmol, arene 30 mL, CO 1 atm, room temperature, 16.5 h, irradiated through Pyrex (>290 nm). [b] The figures in parentheses are the yields (%) based on aldehyde charged. [c] Regioisomeric mixtures. [d] Bibenzyl. [e] 1,2-Diphenylethanol.

the amount of benzyl alcohol is almost equal to the sum of biphenyl and benzophenone. The formation of benzoic acid may be ascribed to aerobic oxidation of benzaldehyde.[17] The formation of benzoin and hydrobenzoin, which were claimed as the products in the photolysis of benzaldehyde in benzene or ethanol,[18] was insignificant. Distillation of a reaction mixture after 16.5 h of irradiation (Rh 0.7 mM) revealed that byproducts of higher boiling point than benzophenone were formed only in a small amount (6.5% of benzaldehyde). Longer reaction time increases the higher boiling point byproducts.

In order to investigate the secondary reactions of aldehyde once formed, aldehydes were added to the carbonylation of toluene or benzene (Table IV). These results clearly show that alcohol and ketone can be formed in situ from aldehyde. The decarbonylation of aromatic aldehydes was negligible, while decarbonylation was a main reaction for cyclohexanecarbaldehyde. The distribution of products largely depends on the nature of aldehyde and solvents. Secondary photoprocesses take place even without the rhodium catalyst. For example, when PhCHO (160 mg) in benzene (30 mL, 50 mM) was irradiated without the catalyst for 16.5 h at room temperature, a mixture of higher boiling point products (147 mg) than benzophenone was formed.

(b) Limit of Aldehyde Yield. When the reaction was carried out in the presence of 0.7 mM RhCl(CO)(PMe₃)₂, the yield of benzaldehyde reached a maximum (60 mM) at about 18 h of reaction time and then gradually decreased. The maximum PhCHO concentration is not simply due to the thermodynamic limitation of eq 1; the argument of thermodynamic limitation is not applicable to the present photoassisted reaction.[19] As a matter of fact, when larger amounts of the catalyst (7 and 35 mM) were employed, a much higher yield of benzaldehyde was achieved (176 and 368 mM, after 94 and 107 h, respectively). The latter concentration of benzaldehyde corresponds to a 3.3% yield based on benzene. The PhCHO concentration remained almost constant thereafter. Two factors are likely to limit the aldehyde yield. One is secondary photoreactions of benzaldehyde once formed (eq 5) (vide supra). The other factor is the decomposition of the catalyst.

$$PhH + CO \xrightarrow[Rh]{h\nu} PhCHO \xrightarrow{h\nu}{(Rh)}$$

$$PhCH_2OH + PhCOPh + PhH + \text{high boiling point products}$$ (5)
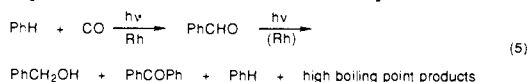
(17) Air had come in through the balloon during the reaction. The concentration of oxygen in the gas phase (balloon) was 0.5% of carbon monoxide after 16.5 h of reaction.

(18) Bradshaw, J. S.; Knudsen, R. D.; Parish, W. W. *J. Chem. Soc., Chem. Commun.* **1972**, 1321–1322.
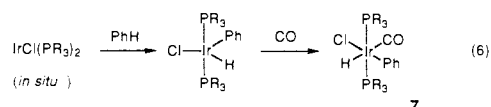
(19) The dehydrogenation of alkane by the same catalytic system proceeds smoothly even under hydrogen atmosphere well exceeding the thermodynamic limitation under the dark conditions; see ref 5p. Energy of photon (78 kcal/mol/einstein at 365 nm) must be a driving force of these thermodynamically unfavorable reactions.
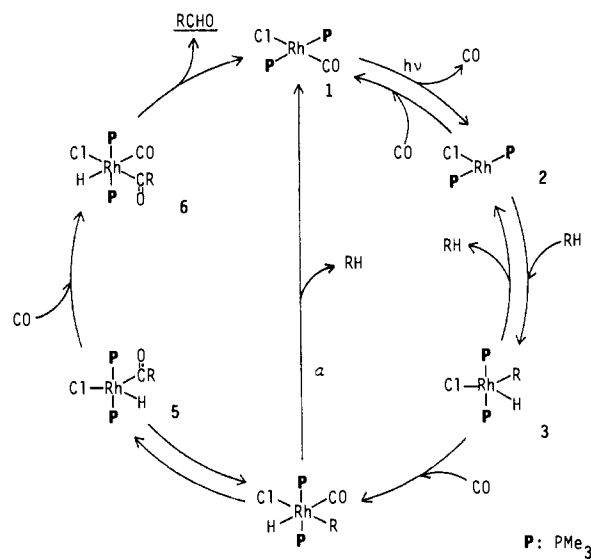
Figure 2. Possible reaction mechanism of carbonylation of hydrocarbons catalyzed by the RhCl(CO)(PMe₃)₂-hν system.

Actually, in a reaction with a 0.7 mM solution of RhCl(CO)-(PMe₃)₂, the MLCT absorption at 360 nm almost disappeared in 20 h to indicate the decomposition of the complex. However, in a reaction with higher Rh concentration (35 mM), more than 60% of the complex did not deteriorated even after 100 h, as monitored with IR absorption of the carbonyl ligand. In this case, the aldehyde yield is presumably limited by the secondary photoreactions of the aldehyde.

(c) Reaction Conditions and Reaction Mechanism. The effects of reaction conditions on the carbonylation rate have been investigated. The higher carbonylation rate or the higher yield of benzaldehyde based on benzene was obtained as the higher concentration of the complex was employed; relative rates to the standard conditions (RhCl(CO)(PMe₃)₂ 0.7 mM in benzene, CO 1 atm, room temperature, 16.5 h) were 0.13 (Rh 0.020 mM) < 0.49 (0.10 mM) < 1.0 (0.70 mM) < 2.6 (7.0 mM). The kinetic order with respect to the rhodium concentration was less than 1, indicating that multinuclear species were not involved in the rate-determining step. Phosphine concentration and CO pressure hardly affected the reaction rate; relative rates were 1.0 (P/Rh = 2), 1.1 (P/Rh = 3), 0.87 (P/Rh = 5), and 1.1 (CO 5 atm, P/Rh = 2). However, high reaction temperature diminished the rate markedly: relative rate 0.081 (80 °C, CO 5 atm, P/Rh = 2).

A possible reaction mechanism is represented in Figure 2. The irradiation of 16-electron Vaska-type rhodium complex **1** results in the formation of 14-electron highly unsaturated complex RhCl(PR₃)₂ (**2**). This elemental step has been well characterized by Ford et al. by flash photolysis.[20] RhCl(PR₃)₂ probably reacts with hydrocarbons to produce hydridoalkyl complex **3**. In fact, the MO calculation reported by Morokuma et al. has suggested that methane easily adds to RhCl(PH₃)₂ affording the hydridomethyl complex.[21] Oxidative addition of benzene to an analogous 14-electron complex, IrCl(PR₃)₂, has been reported by Werner (eq 6).[22] The structure of the resulting hydridophenyl complex

$$IrCl(PR_3)_2 \xrightarrow{PhH} Cl-\underset{PR_3}{\overset{PR_3}{Ir}}\underset{H}{\overset{Ph}{}} \xrightarrow{CO} Cl\underset{PR_3}{\overset{PR_3}{Ir}}\underset{Ph}{\overset{CO}{}}$$ (6)

(in situ)   **7**

determined by X-ray analysis is trigonal bipyramidal with two phosphine in the trans position. The iridium complex was then

(20) Wink, D. A.; Ford, P, C. *J. Am. Chem. Soc.* **1987**, *109*, 436–442. Spillett, C. T.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1932–1933.

(21) Koga, N.; Morokuma, K. *Abstracts*, 35th Symposium on Organometallic Chemistry, Osaka, Japan, 1988, pp 25–27.

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Table V. Carbonylation of Monosubstituted Benzenes (X-C$_6$H$_5$) by RhCl(CO)(PMe$_3$)$_2$[a]

X	concn, mM	yield, %/Rh ArCHO	yield, %/Rh ArCH$_2$OH	selectivity o:m:p
H	7	1540	147	
H	0.7	6520	738	
CH$_3$[b]	7	1530	200	2:64:34
CH$_3$[c]	0.7	3910	3350	1:62:37
CH$_3$O	7	566	93	14:56:30
CH$_3$O	0.7	3930	993	13:53:33
Cl	7	115	37	48:32:20
Cl	0.7	33	4	
NC-	7	82	0	1:85:14
NC-	0.7	65	62	

[a] Rh 0.21 mmol (7 mM) or 0.021 mmol (0.7 mM) in solvent 30 mL, CO 1 atm, room temperature, 16.5 h, irradiated through Pyrex (>290 nm). [b] PhCH$_2$CHO 13%/Rh. [c] PhCH$_2$CH$_2$Ph 2165%/Rh, (CH$_3$C$_6$-H$_4$)$_2$CO 650%/Rh (regioisomeric mixtures).

transformed to a hexacoordinated carbonyl complex 7 under CO. Since an alkyl–rhodium bond is supposed to be weaker than an alkyl–iridium bond, the rhodium complex 4 probably undergoes migratory insertion of CO to give a hydridoacyl complex followed by reductive elimination of aldehyde. Although intermediates at the photoexcited state are likely to be involved in other elemental steps than CO dissociation,[23] further studies on each elemental step are necessary to clarify the details.

As mentioned earlier, we surveyed the phosphine effect in view of the acceleration of C–H oxidative addition (Table I). In practice, however, oxidative addition of C–H bonds does not seem to be the rate-determining step as judged by the following facts: (i) the reaction was not decelerated by the increase of concentration of phosphine or carbon monoxide (vide supra), although oxidative addition should involve a coordinatively unsaturated species; (ii) the kinetic isotope effect (k_H/k_D) evaluated in the reaction with a 1 to 1 mixture of C$_6$H$_6$/C$_6$D$_6$ as a substrate was very small (1.1);[24] and (iii) in the dehydrogenation of cyclooctane by the same catalytic system in an inert solvent, the reaction rate hardly depends on the concentration of cyclooctane.[25]

The phosphine effect shown in Table I may be related to the ease of reductive elimination of hydrocarbons (path a in Figure 2) from the carbonyl complex 4, which presumably is an intermediate from the alkyl complex 3 to the acyl complex 5; Bergman et al. have failed to get Cp*(RCO)IrH(PMe$_3$) by the reaction of Cp*(R)Ir(H)(PMe$_3$) with carbon monoxide because RH was readily eliminated from the latter complex upon treatment with CO.[26] Since the reductive elimination of ethane from PtMe$_3$I-(PR$_3$)$_2$ is depressed in the order PMe$_3$ > PMe$_2$Ph > PMePh$_2$ > PPh$_3$,[27] electron donating and sterically small phosphine is considered to be effective to inhibit the reductive elimination. Thus, the use of a small trialkylphosphine like PMe$_3$ possibly suppresses path a leading to high efficiency of the catalysis. Higher reaction

temperature may enhance the reductive elimination of RH from 4 to result in a lower yield of aldehyde.
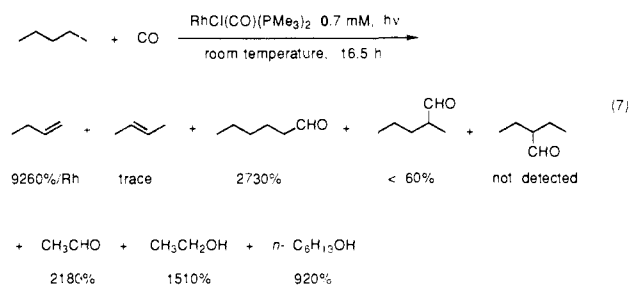
Carbonylation of Substituted Benzenes. Application of the RhCl(CO)(PMe$_3$)$_2$-$h\nu$ system to substituted benzenes is summarized in Table V. Toluene exhibited almost the same reactivity as benzene. On the other hand, the reactivity of anisole was about one-half to one-third as compared with that of benzene. Chlorobenzene and benzonitrile were even less reactive.

In the reaction of toluene (Rh 0.7 mM), a large amount of alcohol was obtained as a byproduct. The hydrogen required for the alcohol formation plausibly came from the methyl group of toluene. A rationale is provided by the formation of a large amount of dibenzyl.

A striking feature of the present carbonylation lies in the unusual regioselectivity as compared with the electrophilic substitution of arenes like the Gatterman–Koch reaction. The isomeric ratio of tolualdehydes formed was ortho:meta:para = 0:2:1. Although the weakest C–H bond is the benzylic one, the formation of phenylacetaldehyde was only about 1% that of tolualdehyde. Jones reported that the oxidative addition of toluene with Cp*Rh(PMe$_3$) yielded hydridotolyl complexes in a similar regioisomeric ratio (ortho:meta:para = 0:2:1).[28] The formation of the hydridobenzyl complex was negligible. On the other hand, Cp*RhH(p-tolyl)(PMe$_3$) easily isomerized even at -10 °C to the meta isomer; the meta/para ratio in equilibrium was approximately 2/1. Judging from these precedents, the regioselectivity of the present carbonylation is explainable on the basis of the thermodynamic stability of hydridoaryl intermediates. Relatively severe steric congestion of the ortho isomer of the hydridoaryl complex makes it less stable than the meta and para isomers. The difference in stabilities between meta and para isomers appears negligible, since the meta/para ratio corresponds to the ratio of the number of C–H bonds. Similar regioselectivities to the present results have been reported in the oxidative addition of toluene to Fe(dmpe)$_2$[29] and in the reaction of toluene with acrylic acid esters catalyzed by Rh$_4$(CO)$_{12}$.[30]

In the carbonylation of anisole, the meta/para ratio was also 2/1. However, a substantially high ortho selectivity was observed as compared with the reaction of toluene. Presumably, this suggests the coordination of methoxy oxygen to rhodium to make the nearby ortho C–H bond more accessible. The lower reactivity of anisole than toluene is also ascribed to the coordination to rhodium. Even poorer reactivity of chlorobenzene and benzonitrile is also considered to be due to the stronger coordination of chloro and cyano groups, respectively. Accordingly, the ortho isomer was the main product in the reaction of chlorobenzene. On the other hand, the strong coordination of the cyano group did not result in increased formation of the ortho isomer in the benzonitrile reaction. This is in agreement with end-on coordination of cyano groups in Rh(I) nitrile complexes.[31]

Carbonylation of Alkanes. The carbonylation of pentane was rather complicated to give C$_6$-aldehydes, C$_6$-alcohols, butenes, acetaldehyde, and ethanol (eq 7). Although pentane has three

$$\text{/\textbackslash\textbackslash/\textbackslash} + CO \xrightarrow[\text{room temperature, 16.5 h}]{\text{RhCl(CO)(PMe}_3)_2 \ 0.7 \text{ mM, } h\nu}$$

9260%/Rh   trace   2730%   < 60%   not detected (7)

+ CH$_3$CHO + CH$_3$CH$_2$OH + n- C$_6$H$_{13}$OH

2180%   1510%   920%

(23) Goldman et al. have very recently revealed that the alkane dehydrogenation by the RhCl(CO)(PMe$_3$)$_2$-$h\nu$ system is a one photon process that requires photoexcitation only in the CO dissociation step from RhCl(CO)-(PMe$_3$)$_2$ (ref 23a below). On the other hand, the studies using excimer lasers have shown that photointensity and wavelength dependences of the carbonylation are quite different from those of the dehydrogenation (ref 23b below). This suggests that the carbonylation needs photoexcitation in other steps than CO dissociation from RhCl(CO)(PMe$_3$)$_2$. (a) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* 1989, *111*, 7088–7093. (b) Moriyama, H.; Sakakura, T.; Yabe, A.; Tanaka, M. *J. Mol. Catal.* 1990, *60*, L9-12. Moriyama, H.; Sakakura, T.; Arakawa, H.; Sakakura, T.; Tanaka, M. *Shokubai* 1989, *31*, 100–103.

(24) A large k_H/k_D value (4.5) has been reported in the reaction of IrH$_2$(RCO$_2$)(PAr$_3$)$_2$ with benzene (see ref 6e). However, small kinetic isotope effects near one have also been observed in the reactions of hydrocarbons with (*t*-BuCH$_2$)Pt(H)(Cy$_2$PCH$_2$CH$_2$PCy$_2$) and Cp*IrH$_2$(PMe$_3$). See: Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, *110*, 1436–1448. Also reference 26.

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(29) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1979, *101*, 1742–1751.
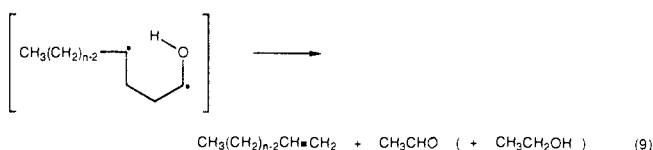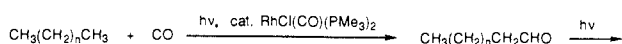
(30) Hong, P.; Mise, T.; Yamazaki, H. *Nippon Kagaku Kaishi* 1985, 479–485.

(31) Maspero, F.; Perrotti, E.; Simonetti, F. *J. Organomet. Chem.* 1972, *38*, C43-C45. Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* 1977, *23*, 1–29.

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kinds of C–H bonds, the regioselectivity of the carbonylation was extremely high; linear aldehyde (hexanal) was selectively obtained. Since the bond energy of alkane C–H bonds decreases in the order of primary > secondary > tertiary, the terminal methyl group should have been the least reactive. Regioselective functionalization of the terminal methyl group of alkanes has been considered to be characteristic of enzymatic reactions. The present system is quite unique in this sense.[6d] High terminal selectivity was also observed in the dehydrogenation[5j] of the acetylene insertion[5o] into alkane C–H bonds by the $RhCl(CO)(PMe_3)_2$-hv system. Dehydrogenation resulting from β-hydride elimination of hydridodalkyl intermediates (3 and 4 in Figure 2) also proceeded as a side reaction to give 1- and 2-pentenes (387 and 716%/Rh, respectively) in the reaction of eq 7. The dehydrogenation under CO was much slower than that under nitrogen (about one-tenth).[5i,p] Dehydrogenation of the alkane followed by hydroformylation of the resulting alkenes (eq 8) is another possible pathway to obtain the aldehyde. However, this possibility is safely ruled out because C_5-aldehydes that should have been formed through this pathway from butenes were not detected at all although a large amount of 1-butene was formed.
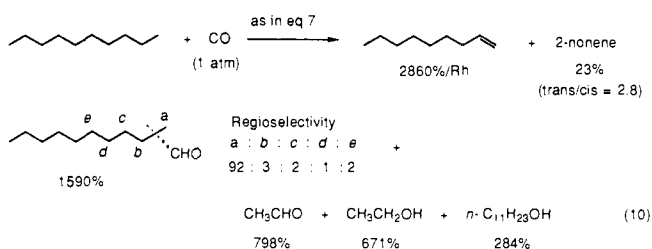
$$RCH_2CH_3 \xrightarrow{-H_2} RCH{=}CH_2 \xrightarrow{H_2,\ CO} RCH_2CH_2CHO \quad (8)$$
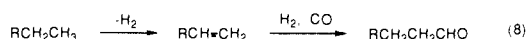
Butenes and acetaldehyde are secondary products formed via Norrish Type II photoreaction of hexanal (eq 9).[32] In practice,

$$CH_3(CH_2)_nCH_3 + CO \xrightarrow{hv,\ cat.\ RhCl(CO)(PMe_3)_2} CH_3(CH_2)_nCH_2CHO \xrightarrow{hv}$$

$$\left[CH_3(CH_2)_{n-2}\overset{\bullet}{-}\overset{H\ \diagdown O}{\underset{\diagup}{\bigtriangleup}}\ \right] \longrightarrow$$

$$CH_3(CH_2)_{n-2}CH{=}CH_2 + CH_3CHO\ (+\ CH_3CH_2OH\ ) \quad (9)$$

irradiation of hexanal (2.5 mmol) in pentane (30 mL) without the catalyst at room temperature for 16.5 h gave 1-butene (1.1 mmol). On the other hand, the formation of propylene and ethylene, which should have been formed through Norrish Type II reaction of 2-methylpentanal and 2-ethylbutanal, was negligible. This is in good agreement with the high regioselectivity of the carbonylation. The high terminal selectivity for the 1-butene formation also agrees with the mechanism of Norrish Type II photoreaction. Distillation of the reaction mixture of eq 7 revealed that the weight of high boiling point (>100 °C (28 mmHg)) byproducts was about half that of hexanal.

The high terminal selectivity of the present system was also realized in the carbonylation of a longer chain n-alkane (decane) (eq 10). The main products were 1-nonene and undecanal. The

$$\text{⋀⋀⋀⋀} + CO \xrightarrow{\text{as in eq 7}} \text{⋀⋀⋀⋀} + \text{2-nonene}$$
$$(1\ atm) \qquad\qquad 2860\%/Rh \qquad 23\%$$
$$\qquad\qquad\qquad\qquad\qquad (trans/cis = 2.8)$$

$$\text{⋀⋀⋀}\underset{d\ \ b}{\overset{e\ \ c\ \ a}{}}\ CHO \qquad \begin{array}{l} \text{Regioselectivity} \\ a : b : c : d : e \\ 92 : 3 : 2 : 1 : 2 \end{array} +$$
$$1590\%$$

$$CH_3CHO + CH_3CH_2OH + n\text{-}C_{11}H_{23}OH \quad (10)$$
$$798\% \qquad 671\% \qquad 284\%$$

terminal selectivity of 1-nonene formation was more than 99%. When a branched alkane (2-methylpentane) was used as a substrate, the less sterically hindered methyl group was preferentially carbonylated to give 5-methylhexanal (eq 11). The carbonylation of cyclohexane was much slower as compared with acyclic alkanes or arenes; the yield of cyclohexanecarbaldehyde and cyclohexanemethanol was 193 and 245%/Rh after 27 h [RhCl-$(CO)(PMe_3)_2$ 0.7 mM, CO 1 atm, room temperature]. However, much higher yields of cyclohexanecarbaldehyde were obtained
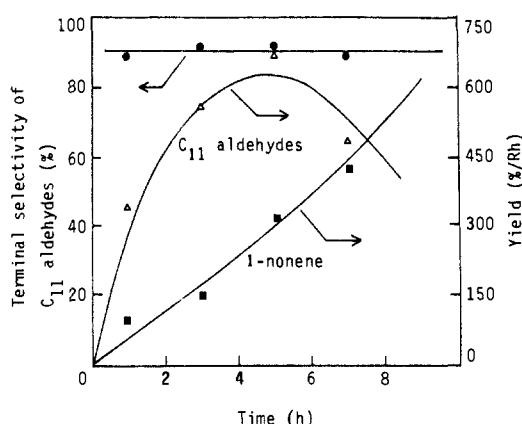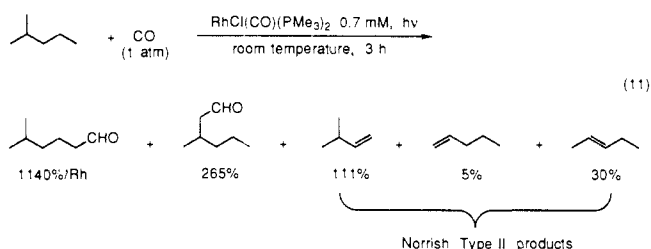
Figure 3. Time dependence of the carbonylation of decane by RhCl-$(CO)(PMe_3)_2$ under irradiation. Reaction conditions: Rh 0.7 mM, CO 1 atm, room temperature, irradiated by a 500-W high-pressure mercury lamp.

when the reaction was conducted in a mixture with benzene (vide infra).

$$\text{⋀⋀⋀} + CO \xrightarrow[\text{room temperature, 3 h}]{RhCl(CO)(PMe_3)_2\ 0.7\ mM,\ hv}$$
$$\qquad (1\ atm)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (11)$$

$$\text{⋀⋀⋀}CHO + \overset{CHO}{\text{⋀⋀}} + \text{⋀⋀} + \text{⋀⋀} + \text{⋀⋀}$$
$$1140\%/Rh \qquad 265\% \qquad 111\% \qquad 5\% \qquad 30\%$$
$$\qquad\qquad\qquad\qquad\qquad \underbrace{\qquad\qquad\qquad\qquad}_{\text{Norrish Type II products}}$$

In addition to the Norrish Type II reaction, various secondary reactions of the initially formed aldehydes may possibly occur under the carbonylation conditions. If this is the case, it is likely that the high terminal selectivity might have come from the rate difference of the secondary reactions of respective regioisomeric aldehydes. However, when we irradiated a mixture of regioisomeric C_{11}-aldehydes in the absence of the rhodium complex, the concentration of each aldehyde decreased at nearly the same rate. Moreover, the high terminal selectivity for the carbonylation of decane was observed constantly from the very beginning of the reaction (Figure 3). Taking these results into account, we can conclude that the high selectivity in the alkane carbonylation is due to the intrinsic regioselectivity of the process and not to the secondary reactions.

Bennett observed the isomerization of $(sec$-alkyl$)IrCl_2(CO)$-$(PPh_3)_2$ to the corresponding n-alkyl complex during the decarbonylation of acyl chloride with $IrCl(PPh_3)_3$.[33] Bergman also reported that regioisomeric hydridopentyliridium complexes, which were formed through oxidative addition of pentane to Cp^*Ir-(PMe_3), isomerized to n-pentyl species upon heating.[26] In addition, analogous isomerization to a primary alkyl complex was much faster for hydridoalkylrhodium complexes, so that secondary alkyl complexes could not be detected in the reactions of n-alkane and $Cp^*Rh(PMe_3)$ even at low temperatures.[34] Hence, high terminal selectivity observed in the carbonylation of n-alkanes may be associated with the thermodynamic stability of the hydridoalkyl intermediates (vide infra) (Figure 2).

Effect of Irradiation Wavelength. In the carbonylation of alkane, primarily formed aldehydes underwent secondary photoreaction (Norrish Type II) to give 1-alkene and acetaldehyde. The absorption maximum of nonconjugated aldehydes appears at about 285 nm.[35] On the other hand, the dissociation of the carbonyl ligand from Vaska-type rhodium complexes is promoted by the irradiation corresponding to the metal-to-ligand charge-transfer

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(34) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346.

(35) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John-Wiley: New York, 1966.

Table VI. Effect of Irradiation Wavelength on the Photoassisted Carbonylation of Decane[a]

entry	wavelength,[b] nm	time, h	C_{9-n}-C(CHO)-C$_n$ (n = 0:1:2:3:4)	nonene[c] 1-	2-
1	295–420	5.0	610 (86:5:4:2:3)	319	0
2	>325	5.0	126 (8:45:17:15:16)	0	0
3	>325	16.5	559 (6:44:17:16:17)	0	0
4	>375	16.5	32 (0:49:18:17:17)	0	0
5[d]	>325	16.5	281 (8:59:13:10:11)	0	0
6[e]	>325	16.5	194 (45:39:7:5:4)	0	0

The column header "yield, %/Rh" spans the last three columns.

[a] RhCl(CO)(PMe₃)₂ 0.0021 mmol, decane 3 mL, CO 1 atm, room temperature, irradiated with a 500-W high-pressure mercury lamp. [b] Ranges where the transmittance of filter is over 10%. [c] Octenes were not detected. [d] RhCl(CO)(PBu₃)₂ was used as the catalyst. [e] RhCl-(CO)[P(i-Pr)₃]₂ was used as the catalyst.

Table VII. Effect of Wavelength on the Carbonylation of Benzene and Toluene[a]

substrate	wavelength,[b] nm	product, %/Rh
benzene	295–420	PhCHO, 283; PhCH₂OH, 6
	>325	PhCHO, 54
	>375	PhCHO, trace
toluene	295–420	tolualdehyde, 334 (o:m:p = 0:66:34) phenylacetaldehyde, trace methylbenzyl alcohols, 592
	>325	tolualdehyde, 129 (o:m:p = 0:70:30) phenylacetaldehyde, 175 methylbenzyl alcohol, 30

[a] RhCl(CO)(PMe₃)₂ 0.0021 mmol, benzene 3 mL, CO 1 atm, room temperature. [b] Ranges where transmittance of filter is over 10%.

(MLCT) band around 365 nm.[10,20] This MLCT band coincides well with the strongest irradiation wavelength of the high-pressure mercury lamp (366 nm). Hence, if we cut off the short-wavelength region capable of aldehyde excitation, suppression of the Norrish Type II reaction is expected while the excitation of the MLCT is still available.

The effect of irradiation wavelength on the carbonylation of decane with RhCl(CO)(PMe₃)₂ is summarized in Table VI. Irradiation was carried out with a lamp-housed high-pressure mercury lamp equipped with glass filters to regulate the wavelength. When irradiation involving short-wavelength light around 300 nm was applied (entry 1), terminal selectivity of the carbonylation was high to give undecanal with the concomitant formation of 1-nonene; the result is similar to the reaction using an immersion type lamp through Pyrex (eq 10). On the other hand, when the longer wavelength light (>325 nm) irradiated the system, the Norrish Type II reaction leading to 1-nonene formation was completely suppressed as anticipated. To our surprise, however, the regioselectivity of the carbonylation was lost at the same time, and 2-methyldecanal became the main product. In addition, the shorter wavelength light appears more effective in obtaining high catalytic activity; when the shorter wavelength light was cut off, the turnover rate decreased to one-fifth (entries 1 and 2). The catalytic activity further decreased when the still longer wavelength light was applied (entry 4). The terminal selectivity could be recovered to some extent by the use of a bulky phosphine ligand like triisopropylphosphine (entry 6), even though the shorter wavelength light was absent.

Short-wavelength light around 300 nm was also important in obtaining high catalytic activity for the carbonylation of benzene and toluene (Table VII). The importance of short-wavelength light in obtaining a high catalytic activity was also clearly confirmed by using excimer lasers.[23b] In addition to this, the regioselectivity of carbonylation of toluene markedly depended on the wavelength. In the presence of short-wavelength light, the regioselectivity was very similar to that obtained with an immersion type lamp (Table V) (o:m:p = 0:2:1). Carbonylation at the benzylic methyl group to give phenylacetaldehyde was negligible as compared with that at the aromatic ring. On the other hand,

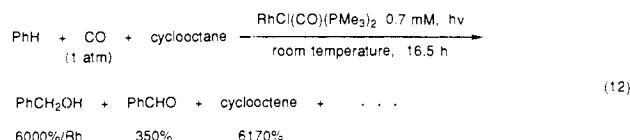**Table VIII.** Competitive Carbonylation of Various Alkanes with Benzene by RhCl(CO)(PMe₃)₂ under Irradiation[a]

substrate	products, %/Rh	rel reactivity to benzene[b]
cyclohexane	PhCHO, 1070; PhCH₂OH, 562 cyclohexanecarbaldehyde, 1420 cyclohexyl phenyl ketone, 429[c] cyclohexene, 150	0.59
pentane	PhCHO, 1230; PhCH₂OH, 302 C$_n$-C(CHO)-C$_{4-n}$, 497 (n; 0:1:2 = 19:53:28) 1-butene, 21	0.13
decane	PhCHO, 1070; PhCH₂OH, 738 C$_n$-C(CHO)-C$_{9-n}$, 825 (n; 0:1:2:3:4 = 8:22:25:22:23) 1-nonene, 21; 1-octene, 25	0.11
cyclooctane	PhCHO, 480; PhCH₂OH, 459 cyclooctanecarbaldehyde, 109 cyclooctene, 721	0.05

[a] Rh 0.021 mmol, 1 to 1 mixture (mol/mol) of benzene and a substrate 30 mL, CO 1 atm, room temperature, 2 h, irradiated through Pyrex (>290 nm). [b] Normalized per C–H. [c] Postulated to be formed from benzene and cyclohexanecarbaldehyde via cyclohexanecarbonyl radical in order to calculate the relative reactivity.

cutting off the light around 300 nm resulted in an increase in the selectivity for phenylacetaldehyde formation.

When short-wavelength light around 300 nm does not exist, the regioselectivity seems to be kinetically controlled. Hence, the carbonylation takes place at the weakest C–H bond, i.e., the secondary C–H bond in decane and the benzylic C–H bond in toluene. On the other hand, since the irradiation involving short-wavelength light resulted in carbonylation at the primary C–H bond of decane and the aromatic C–H bond of toluene, it is envisaged that the reaction is thermodynamically controlled via the most stable hydridoalkyl (or aryl) intermediate. These results are rationalized as follows. Oxidative addition of hydrocarbons is likely to occur at every C–H bond, preferably at weaker secondary or benzylic C–H bond. The resulting hydridoalkyl (or aryl) complexes, however, isomerize to thermodynamically stable C–H adducts. The existence of short-wavelength light may accelerate the isomerization and make it faster than CO insertion to a carbon–metal bond.

Competitive Carbonylation. Relative reactivities of various hydrocarbons in the present carbonylation were examined in competitive reactions with use of a 1 to 1 (mol/mol) mixture of benzene and a hydrocarbon as a substrate (Table VIII). The reactivity order was benzene > cyclohexane > pentane ≈ decane > cyclooctane. In these reactions, terminal selectivity for n-alkane was not achieved, presumably because short-wavelength light around 300 nm was cut off by benzene. Little occurrence of Norrish Type II reaction also corresponds to the lack of short-wavelength light. When cyclohexane was carbonylated in a mixture with benzene, cyclohexanecarbaldehyde was obtained much more effectively as compared with the reaction of cyclohexane alone (vide supra). This phenomenon may be partly due to a small occurrence of secondary photoreactions of cyclohexanecarbaldehyde including decarbonylation (Table IV) because of the filter effect of benzene. When benzene was carbonylated in a mixture with an alkane, the benzyl alcohol/benzaldehyde ratio was enhanced; the ratio reaction 17 after 16.5 h in a reaction with cyclooctane (eq 12). This indicates the possibility of reductive carbonylation of hydrocarbons to produce an alcohol.

$$\text{PhH} + \text{CO} + \text{cyclooctane} \xrightarrow[\text{room temperature, 16.5 h}]{\text{RhCl(CO)(PMe}_3)_2 \ 0.7 \text{ mM, hv}}$$
$$\text{(1 atm)}$$

$$\text{PhCH}_2\text{OH} + \text{PhCHO} + \text{cyclooctene} + \cdots \qquad (12)$$
$$6000\%/\text{Rh} \quad\quad 350\% \quad\quad 6170\%$$

In summary, we have demonstrated the direct carbonylation of hydrocarbons including alkanes by homogeneous catalysis. The most fascinating feature of the catalytic system is its unique regioselectivity, especially the high terminal selectivity in the

Table IX. List of New Complexes

complex	color	mp with dec, °C	ν_{C-O},[a] cm⁻¹
RhCl(CO)[CH₃PCH₂CH(CH₃)CH(CH₃)CH₂]₂	yellow	71–73	1959
RhCl(CO)[CH₃PCH₂C(CH₃)=C(CH₃)CH₂]₂	yellow	108–110	1951
RhCl(CO)[P(CH₂O)₃CCH₃]₂	yellow	141–145	2000[b]
Rh(SCN)(CO)(PMe₃)₂	yellow	113–114	1976 / 2085 (SCN)
Cl(CO)Rh(Me₂PCH₂PMe₂)₂Rh(CO)Cl[c]	orange	170–180	1962
RhF(CO)[P(*p*-tolyl)₃]₂[d]	yellow	177–180	1961
RhBr(CO)[P(*p*-tolyl)₃]₂	yellow	178–180	1974
RhI(CO)[P(*p*-tolyl)₃]₂	yellow		1976
Rh(OH)(CO)[P(*p*-tolyl)₃]₂	yellow	142–144	1950
Rh(CN)(CO)[P(*p*-tolyl)₃]₂	yellow	148–150	1994 / 2125 (CN)
Rh(SCN)(CO)[P(*p*-tolyl)₃]₂	yellow	192–195	1988 / 2091 (SCN)
AcCo(CO)₃(PEt₃)	yellow	31	1967, 1989[b]

[a] Nujol mull. [b] Benzene solution. [c] ³¹P NMR (CDCl₃) δ −4.3 (d, J = 117 Hz). [d] ³¹P NMR (C₆D₆) δ 22.75 (d, J = 142 Hz); the corresponding chloro complex, δ 26.79 (d, J = 127 Hz).

carbonylation of *n*-alkanes. Utilization of sunlight as an irradiation source and application to various functionalized substrates are additional interesting subjects.

Experimental Section

Electronic spectra were recorded on a Shimadzu UV-3100 spectrometer. Infrared spectra were obtained on a Jasco A-302 spectrometer. ¹H and ³¹P NMR were measured on a Hitachi R-40 (90 MHz) and a JEOL FX-90A (90 MHz) spectrometer. Mass spectra were recorded on a Shimadzu QP-1000 or a JEOL JMS-D300 GC-MS spectrometer. Products were characterized by GC and GC-MS; capillary columns, Shimadzu OV-1 (25 m), Shimadzu OV-1701 (25 m), Gasukuro Kogyo PEG-20M (25 m), and Hitachi DDP-90 (90 m); packed columns, Gasukuro Kogyo PEG-20M (1 m), VZ-7 (5 m), and OV-101 (1 m). Gaseous products were analyzed by a fuel gas analysis system, Gasukuro Kogyo Model 373FG. Yields were evaluated by GC analysis of reaction mixtures with an internal standard (*β*-methylnaphthalene or dibenzyl).

Transition-Metal Complexes. RhCl(CO)(PMe₃)₂ was prepared by a modified procedure of the literature method[36] as follows. Trimethylphosphine (1.7 g, 22 mmol) was added dropwise to a solution of [RhCl(CO)₂]₂ (1940 mg, 10 mmol) in benzene (10 mL) at room temperature under nitrogen. Evolution of carbon monoxide was observed along with the formation of yellow precipitate. After 1 h, the reaction mixture was concentrated in vacuo at room temperature. The resulting yellow solid dissolved in hot MeOH (25 mL) was cooled very slowly to 0 °C. The large yellow prism formed was washed at −50 °C first with MeOH and then with hexane and was dried in vacuo to afford 2.3 g (71%) of RhCl(CO)(PMe₃)₂. Cooling of the mother liquid from the MeOH recrystallization to −50 °C gave an additional 0.65 g of the complex. The melting point,[36,37] IR,[38] and ¹H and ³¹P NMR[37] spectra were all identical with those reported in the literature.

RhCl(CO)[P(CH₂O)₃CMe]₂, RhCl(CO)(PBu₃)₂,[39] RhCl(CO)[P(*i*-Pr)₃]₂,[40] RhCl(CO)[P(OMe)₃]₂,[41] RhCl(CO)(dppe),[42] Cl(CO)Rh(Me₂PCH₂PMe₂)₂Rh(CO)Cl, RhCl(CO)[CH₃PCH₂C(CH₃)=C(CH₃)CH₂]₂,[43] and RhCl(CO)[CH₃PCH₂CH(CH₃)CH(CH₃)CH₂]₂[43] were prepared similarly.

[RhCl(CO)₂]₂,[44] Rh₄(CO)₁₂,[45] Cp*Rh(CO)₂,[46] RhCl(CO)(PPh₃)₂[47]

RhCl(CO)[P(*p*-tolyl)₃]₂,[47,48] RhF(CO)[P(*p*-tolyl)₃]₂,[49] IrCl(CO)(PMe₃)₂,[50] IrCl(CO)(PPh₃)₂,[51] Fe(CO)₃(PMe₃)₂,[52] Ru(CO)₃(PPh₃)₂,[53] CoCl(CO)₂(PPh₃)₂,[54] [Co(CO)₃(PEt₃)]₂,[55] AcCo(CO)₃(PEt₃),[56] IrH₅[P(*i*-Pr)₃]₂,[57] Ni(CO)₂(PPh₃)₂,[58] Pt(CO)₂(PPh₃)₂,[59] and Pt(CO)(PPh₃)₃[59] were prepared according to the literature method. RhX(CO)[P(*p*-tolyl)₃]₂ (X = Br, I, SCN, CN, OH) and Rh(SCN)(CO)(PMe₃)₂ were prepared from the corresponding fluoride and chloride complexes through anion exchange.[48,49,60] RhCl(CO)₂P(*p*-tolyl)₃[61] (IR 2091 and 2007 cm⁻¹) was prepared in situ from [RhCl(CO)₂]₂ and P(*p*-tolyl)₃ and used without isolation.

All new compounds gave satisfactory elemental analyses. Carbonyl stretching bands of new complexes were summarized in Table IX.

Typical Reaction Procedure. RhCl(CO)(PMe₃)₂ (6.7 mg, 0.021 mmol) was dissolved in benzene (30 mL) under nitrogen in a Pyrex flask to make a 0.7 mM solution. The solution was freeze-thaw degassed (twice), and carbon monoxide was introduced into the reaction vessel from a balloon filled with CO. The solution was irradiated with a 100-W high-pressure mercury lamp (Riko, UVL-100H) through a Pyrex cooling jacket with magnetic stirring at an ambient temperature. The wavelength range where transmittance is over 10% is >290 nm. The flask was surrounded by mirror to enhance irradiation efficiency. This was effective when the rhodium concentration was high (e.g. 7 mM).

The other substrates were carbonylated in a similar manner. Products were identified by the comparison of GC retention times and fragmentation patterns of GC-MS with authentic samples.

Isolation of Benzaldehyde. A solution of RhCl(CO)(PMe₃)₂ (1.05 mmol) in benzene (30 mL) was irradiated according to the typical procedure for 107 h at room temperature. The GC analysis of the solution revealed the formation of benzaldehyde (1171 mg). The reaction mixture was concentrated in vacuo. Resulting brown oil was purified by silica gel column chromatography (Et₂O:hexane = 1:20) followed by Kugelrohr distillation (110 °C (30 mmHg)) to give pure benzaldehyde (726 mg). The aldehyde was fully characterized by GC-MS, IR, and NMR.

Estimation of the Formation of High Boiling Point Byproducts. Benzene (30 mL) was subjected to carbonylation in the presence of

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RhCl(CO)(PMe₃)₂ (6.7 mg) according to the typical procedure (room temperature, 16.5 h) to give 159 mg of benzaldehyde. The reaction mixture was distilled under reduced pressure to remove benzene and low-boiling products (up to 200 °C (28 mmHg), Kugelrohr); the boiling point of benzophenone is 185 °C (28 mmHg). The weight of the residue was only 12.5 mg. Since the residue must have contained at least 2.2 mg of Rh metal coming from 6.7 mg of the starting complex, the amount of higher boiling products is estimated to be less than 10.3 mg (only 6.5% of benzaldehyde). A similar analysis for pentane carbonylation (room temperature, 16.5 h) revealed that the weight of higher boiling point products (>100 °C (28 mmHg)) was 55% of hexanal.

H/D Exchange of Ligated PMe₃. Benzene-d_6 was carbonylated with RhCl(CO)(PMe₃)₂ according to the typical procedure. The reaction mixture was analyzed by GC-MS (EI) to estimate the extent of deuteration of RhCl(CO)(PMe₃)₂ (packed column OV-1, 1 m). RhCl(CO)(PMe₃)₂-d_0 showed the parent ions at m/z 318 (^{35}Cl) and 320 (^{37}Cl) in the ratio of 3:1, while the complex having n deuteriums exhibited its parent ions at (318 + n) and (320 + n).

Typical Procedure for Wavelength-Controlled Experiment. A 0.7 mM solution of RhCl(CO)(PMe₃)₂ in benzene was placed in a Pyrex rectangular cell (1 cm) under nitrogen. The solution was degassed under vacuum and then filled with carbon monoxide (1 atm, balloon). This process was repeated several times to exclude nitrogen. The solution was irradiated with a 500-W high-pressure mercury lamp (Ushio, USH-500D) at room temperature. The wavelength was regulated by means of glass filters (Toshiba, UV-D35, UV-35, and L-39). Wavelength ranges of these glass filters (ranges where the transmittance is over 10%) are 295–420, >325, and >375 nm, respectively.

Effect of CO Pressure and Temperature. A 0.7 mM solution of RhCl(CO)(PMe₃)₂ in benzene (15 mL) was placed under nitrogen in a Hastelloy-C autoclave with a Pyrex window. The nitrogen atmosphere was replaced with carbon monoxide through pressurization (70 atm)–depressurization cycles. The solution was irradiated with a 500-W high-pressure mercury lamp (Ushio, USH-500D), while temperature was controlled with plate heaters attached to the side of the autoclave.

Evidence for a Bis(alkylidene)silacyclopropane Intermediate in the Platinum-Mediated Formation of a Silacyclobutene

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Abstract: When Ph₂Si(C≡CCMe₃)₂ is treated with a cationic Pt–H reagent, a 4-alkylidene-1-silacyclobutenyl ring system is formed. Evidence for the presence of two intermediates in this reaction sequence is obtained by using selective trapping reactions. Acetic acid cleaves at Pt–C bond to give alkenylsilane products, indicating the intermediate formation of a Pt, Si-μ-alkenylidene complex. ROH reagents react with a proposed bis(alkylidene)silacyclopropane intermediate to initiate ring opening and to form η³-butadienyl complexes (where R = H, Me, Et, or Ph). The structure of one of these complex ions (R = H) has been confirmed by X-ray crystallography.

Small-ring, organosilacyclic compounds are of special interest as reagents for the preparation of larger cyclic molecules or new materials due to the greater stability of these compounds relative to that of the corresponding carbocyclic compounds.[2] Silacyclobutenes undergo cycloaddition and various ring-opening reactions of interest; however, general and convenient synthetic methods for the preparation of silacyclobutenes are not available.[2–4] In recent work by Fink and co-workers, silacyclobutenes and a long-lived *o*-silaxylylene intermediate have been prepared from silacyclobutadienes.[5] In addition, the Ishikawa and Higuchi groups have prepared several analogous and highly substituted (*exo*-alkylidene)silacyclobutenes from either catalytic or stoichiometric reactions involving Ni(0) or Ni(II) species in the reaction of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene. These selected (*exo*-alkylidene)silacyclobutenes are formed under high reaction temperatures (135-200°C for 15-21h), and they react with methanol to form various methoxysilacyclobutenes.[6]

We reported recently a facile, *low-temperature* synthesis of an (*exo*-alkylidene)silacyclobutenyl ring system from readily available dialkynylsilane-utilizing platinum-mediated addition and insertion reactions.[7] Specifically, when the dialkynylsilane, **1**, is treated with the platinum hydride complex, **2**, under anhydrous conditions, the silacyclobutenyl complex **5** is isolated in good yield (see Scheme I). The molecular structure of **5** has been confirmed by X-ray crystallography.[7]

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