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Thermal Activation of Alkane C-H Bonds by Palladium Catalysts. Carbonylation of Alkanes with Carbon Monoxide

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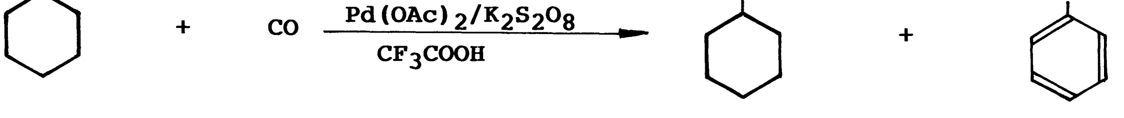
The reaction of cyclohexane with 30 atm CO at 80 °C by using the Pd(OAc)$_2$/CF$_3$COOH catalyst system without irradiation gives rise to cyclohexanecarboxylic acid in 195% yield based on Pd with a small amount of benzoic acid. The reactions of cycloheptane and n-hexane give similar results. This constitutes the first example of carboxylation of alkanes with CO by transition metal complexes without irradiation.

There is now a great deal of interest in exploring new reactions via C-H bond activation by transition metal complexes.$^{1)}$ Generally two methods for the C-H bond activation by metal complexes are so far known: one is by electrophilic substitution and the other by oxidative addition. Recently, Tanaka has developed several interesting alkane C-H bond activation reactions by irradiation of Rh/phosphine based catalysts utilizing oxidative addition.$^{2)}$ We have discovered the palladium-catalyzed substitution reaction of olefins by aromatic compounds to give aromatic-substituted olefins which proceeds via an ArPdL sigma complex intermediate derived from direct thermal activation of a C-H aromatic bond by electrophilic substitution by Pd(II).$^{3)}$ In continueing efforts to explore reactions involving C-H bond activation by transition metals, we investigated the thermal activation of alakne C-H bonds by transition metal complexes. Here we report our results on the palladium(II)-catalyzed carboxylation of alkanes such as cyclohexane, cycloheptane, and n-hexane with CO, through thermal C-H bond activation.

Heating cyclohexane (10 ml) and Pd(OAc)$_2$ (3 mmol) in CF$_3$COOH (20 ml) and MeOH (3 ml) with K$_2$S$_2$O$_8$ (9 mmol) under 30 atm CO at 80 °C for 20 h resulted in the formation of cyclohexanecarboxylic acid (**1**) in 195% yield based on Pd with a small amount of benzoic acid (**2**) (0.2%). This is the first example of carboxylation



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of alkane through thermal activation with transition metals without irradiation.

Since we have found that the direct carboxylation reaction of substituted benzenes with CO by $Pd(OAc)_2$ affording arenecarboxylic acids, is electrophilic with ortho-para orientation when an electron-donating group is attached to the benzene ring,$^{4)}$ the present carboxylation reaction likely also proceeds electrophilically.$^{5)}$ Table 1 summarizes the results of the reactions of cyclohexane with CO under various conditions. As can be seen from the table, substitution of CF_3COOH with CH_3COOH gives no carboxylation products (run 1 vs 2). Of the oxidants examined, potassium persulfate is the best and cerium ammonium nitrate and sodium nitrate have no considerable effect. Addition of MeOH to CF_3COOH greatly increases the yield of acid (**1**) (run 7), and longer reaction period and higher reaction temperature both increase the yield (runs 6 vs 8 and 9).

Table 1. Carboxylation of cyclohexane with carbon monoxide$^{a)}$

Run	Solvent (ml)	Oxidant (mmol)	Yield/%$^{b)}$ **1**	**2**
1	AcOH (7)$^{c)}$	-	0	0
2	CF_3COOH (7)	-	0.1	0
3	CF_3COOH (14)	$Ce(NO_3)_4 \cdot 2NH_4NO_3$ (9)	0.2	0$^{d)}$
4	CF_3COOH (14)	$NaNO_3$ (9)	0.4	0.3
5	CF_3COOH (14)	p-Benzoquinone (12)/ MnO_2 (12)	0.1	0
6	CF_3COOH (14)	$K_2S_2O_8$ (9)	19	0.1
7	CF_3COOH (20) MeOH (3)	$K_2S_2O_8$ (9)	195	0.2
8	CF_3COOH (7)	$K_2S_2O_8$ (9)$^{e)}$	119	0.2
9	CF_3COOH (7)	$K_2S_2O_8$ (9)$^{f)}$	74	0.1

a)$Pd(OAc)_2$ 3 mmol, 30 atm CO at 80 °C for 20 h. b)Based on Pd. c)1 atm CO. d)Nitrocyclohexane was also formed in 12% yield. e)30 h. f)180 °C.

Similarly, cycloheptane and n-hexane react with CO to give carboxylic acids. In the case of n-hexane, corresponding 1-, 2-, and 3-carboxylic acids were obtained in 2:29:20 molar ratio, which is a marked contrast to the case of $RhCl(CO)(PMe_3)_2$ with irradiation in which the terminal carbon is selectively carbonylated.$^{6)}$ This result suggests that the present reaction proceeds by electrophilic attack of $Pd^+(CF_3COO)$ to alkane (R-H) to give $R\text{-}PdOCOCF_3$ intermediate.

References

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