

Novel Role of Carbon Monoxide as a Lewis Acid Catalyst for Friedel–Crafts Reaction

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The Friedel–Crafts reaction, in which a Lewis acid plays a crucial role to improve the efficiency of the reaction, is the most important and traditional method to introduce an alkyl group into an aromatic ring.¹ Thus far, a gaseous Lewis acid, such as BF_3 , has been employed as a very useful Lewis acid due to the simple separation from the reaction mixture, despite its corrosive and expensive nature. Thus, a gaseous, noncorrosive, and inexpensive Lewis acid would allow us to construct an economical and environmentally-friendly process. In the course of our studies on the reaction of propargyl electrophiles with low valent transition-metal complexes,² we observed the occurrence of an unanticipated Friedel–Crafts reaction under a carbon monoxide pressure, and it was not mediated by metal complexes. This seems to bear some relation to the fragmentation of alkoxyhalocarbenes to carbon monoxide and haloalkanes (Scheme 1, plain arrow), in which the generation of carbocations is proposed as a key step.³ Following the fragmentation sequence in the reverse direction led us to propose that carbon monoxide potentially could play an important role as a gaseous, noncorrosive, and inexpensive Lewis acid to generate alkyl cation. Here, we describe for the first time a novel role of carbon monoxide as a Lewis acid for Friedel–Crafts reactions (Scheme 1, **bold arrow**).

The reaction of benzyl chloride in benzene either under a carbon monoxide pressure (10 atm) or under a nitrogen atmosphere in an autoclave fitted with a glass insert tube was examined.⁴ Friedel–Crafts alkylation reaction proceeded at 130 °C under carbon monoxide pressure to give diphenylmethane in excellent yield (Table 1). On the other hand, the reaction under a nitrogen atmosphere did not proceed at all. The reaction with toluene also afforded a mixture of Friedel–Crafts products. The reaction under one atmospheric pressure of carbon monoxide also proceeded quantitatively, but prolonged time was required.⁵ Similarly, under carbon monoxide pressure, *p*-methylbenzyl chloride underwent Friedel–Crafts reaction in benzene at 130 °C or in toluene at 90 °C. The reaction of 3-phenylpropargyl chloride with benzene proceeded under the same conditions to give chlorocinnamyl benzene by addition of hydrogen chloride to the triple bond of a simple Friedel–Crafts product,⁶ which is

Scheme 1. Possibility of Carbon Monoxide as a Lewis Acid

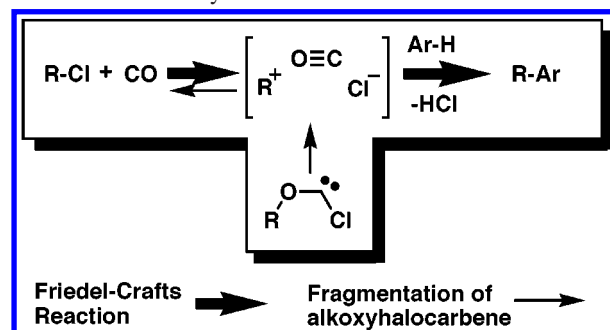


Table 1. Carbon Monoxide-Catalyzed Friedel–Crafts Reaction

electrophile	conditions	product, yield ^a
	benzene CO 10 atm 130 °C 10 h	95%
	toluene CO 10 atm 130 °C 10 h	59% 29%
	toluene CO 1 atm ^b 130 °C 30 h	67% 33%
	benzene CO 10 atm 130 °C 10 h	91%
	toluene CO 10 atm 90 °C 10 h	60% 40%
	benzene CO 10 atm 130 °C 10 h	13% 86% (E/Z = 69/31)
	toluene CO 20 atm 150 °C 30 h	50% 10%

^a Isolated yield. ^b Bubbling CO for 2 min at 0 °C.

a highly atom-economic reaction. Friedel–Crafts acylation of hydrocinnamoyl chloride with toluene also proceeded, although more severe conditions were needed.⁷ The isolation of the reaction product is extremely easy; after the release of carbon monoxide in a well-ventilated fume hood, only evaporation of the solvent gave isolated products, since carbon monoxide is a gaseous Lewis acid and does not undergo such complexation with HCl to transform the Lewis acid to nonvolatile compounds as ordinary Lewis acids do.

To confirm the role of carbon monoxide, control reactions were carried out, and the results are summarized in Table 2. The reaction of benzyl chloride in benzene-*d*₆ under carbon monoxide pressure (5 atm) in a pressure NMR tube at 130 °C for 10 h proceeded smoothly to give diphenylmethane-*d*₅ in 95% yield (run 1). To rule out the possibility that a pressurized atmosphere promotes the reaction, the same reaction was attempted under a

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(4) A solution of electrophile in benzene or toluene (66.4 mM) was placed into a glass insert tube in an autoclave, then was pressurized with carbon monoxide and heated at 130 °C or 90 °C for 10 h. Without a glass insert tube, reaction proceeded under a nitrogen atmosphere, since the oxidized autoclave inside wall could act as a Lewis acid to promote Friedel–Crafts reaction.

(5) A solution of benzyl chloride in toluene was placed into a pressure-resistant glass tube, and carbon monoxide was bubbled into the solution for 2 min at 0 °C. Then, the solution was heated at 130 °C for 30 h.

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Table 2. Control Reactions

$$\text{Ph-CH}_2\text{Cl} \xrightarrow{\text{C}_6\text{D}_6, 130\text{ }^\circ\text{C}} \text{Ph-CH}_2\text{C}_6\text{D}_5$$

run	conditions	yield
1	CO 5 atm, 10 h	95%
2	N ₂ 5 atm, 10 h	no reaction
3	CO ₂ 5 atm, 10 h	no reaction
4	Fe(CO) ₅ 5 mol% N ₂ 1 atm, 17 h	30%
5	Fe(CO) ₅ 5 mol% CO 5 atm, 17 h	10%

^a NMR yield.

pressurized atmosphere of nitrogen (run 2) or carbon dioxide (run 3), but in vain. Moreover, the same reaction was examined in the presence of a catalytic amount of Fe(CO)₅, since iron pentacarbonyl, Fe(CO)₅, could be generated in a carbon monoxide cylinder⁸ and metal carbonyl complexes could be a catalyst for Friedel–Crafts reaction.⁹ In fact, Fe(CO)₅ did catalyze the reaction (run 4); however, the yield was much lower than that in run 1.¹⁰ Moreover, under carbon monoxide pressure the reaction proceeded much more slowly (run 5), which rules out the possibility that Fe(CO)₅ catalyzes the reaction in run 1 and indicates that carbon monoxide acts as a Lewis acid for Friedel–Crafts reaction.

(8) Carbon monoxide cylinder stability test in SUMITOMO SEIKA CHEMICALS CO., LTD.

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Most of studies on carbon monoxide concern the efficiency of incorporation of carbon monoxide into organic compounds; however, thus far, the application of carbon monoxide as a reaction promoter has not been studied at all. Thus, the new aspect of carbon monoxide reported here for the first time as a noncorrosive, economical, and easily re-collectable gaseous, smallest Lewis acid is very important from the viewpoints of organic, physical, industrial, theoretical, combinatorial, and green chemistry. Moreover, it would not only allow us to construct new reactions catalyzed by carbon monoxide but also require us to reconsider the role of carbon monoxide in the reported reactions under carbon monoxide atmosphere. Further efforts related to this reaction including kinetic and computational studies are under progress in this laboratory.

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(10) A solution of benzyl chloride (6.3 mg, 0.05 mmol) in 0.5 mL of C₆D₆ was pressurized with carbon monoxide (5 atm) and heated at 130 °C for 10 h in a pressure-resistant NMR tube. For the reactions in the presence of 5 mol % of Fe(CO)₅, 0.5 mg of Fe(CO)₅ was added. NMR yields are given. In control reactions, carbon monoxide compressed into a cylinder in a month was used, in which less than 0.52 ppm of Fe(CO)₅ was generated.⁸ This concentration corresponds to the presence of less than 0.005 mol% of Fe(CO)₅ in run 1.