Rhenium Complexes-Catalyzed Alkylation of Arenes with Alkyl Halides

Yutaka Nishiyama,* Fujio Kakushou, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680

Rhenium complexes have been shown to catalyze the alkylation of arenes with alkyl halides. When arenes were reacted with an alkyl chloride in the presence of a catalytic amount of rhenium complexes, such as bromopenta-carbonylrhenium(I) [ReBr(CO)$_5$], tricarbonylcyclopentadienylrhenium(I) [Re(C$_5$H$_5$)(CO)$_3$] and decacarbonyldirhenium [Re$_2$(CO)$_{10}$], alkylation of the arenes proceeded under mild conditions to give a mixture of mono- and dialkyl substituted arenes in moderate-to-good yields.
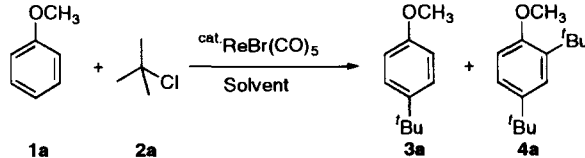
The Friedel–Crafts alkylation of arenes is one of fundamental and useful reactions in organic and industrial chemistry. Various Lewis and protonic acids or solid acid catalysts have been used for the alkylation of arenes with alkyl halides, alkenes or alcohols; however, most of the previously reported methods were usually carried out under strongly acidic conditions.[1] The development of a catalytic method, in which the reaction proceeds under weakly acidic or neutral conditions, was then to be explored with respect to both synthetic and environmental aspects. There has recently been increasing interest in the development of a transition-metal-based Lewis catalyst,[2,3] because it is expected that control of the Lewis acid acidity and the stereoselectivity would be easily achieved by replacing the ligands of the complexes or by using chiral complexes. Thus catalytic applications of rhenium compounds have recently attracted much attention in organic synthesis. Although many studies on the MeReO$_3$-catalyzed oxidation of organic compounds have been reported,[4,5] few have addressed the catalytic use of rhenium complexes in another reactions.[6] Recently, Narasaka et al. have shown the rhenium-catalyzed acylation of arenes with acyl halides.[6b]

In the present study, the alkylation of arenes with alkyl halides in the presence of a catalyst involving rhenium complexes was examined in order to understand the catalytic activity of rhenium complexes as a transition metal-based lewis-acid catalyst.[7]

Results and Discussion

When anisole (1a) was reacted with 3 equiv amounts of t-butyl chloride (2a) in the presence of a catalytic amount of bromopentacarbonylrhenium(I) [ReBr(CO)$_5$] (0.01 equiv) in 1,2-dichloroethane (3.5 mL) at 84 °C for 0.5 h, a mixture of a monoalkylated product, 4-t-butylanisole (3a), and a dialkylated product, 2,4-di-t-butylanisole (4a), was formed in almost quantitative yields (3a : 4a = 66 : 34) (Entry 3 in Table 1). The results of the alkylation of 1a with 2a under various reaction conditions are given in Table 1, which contain

Table 1. ReBr(CO)$_5$-Catalyzed Reaction of Anisole with ^{t}BuCl under Various Reaction Conditions$^{a)}$

Entry	Solvent	Temp/°C	Time/h	Yield/% (3a : 4a)$^{b),c)}$
1	ClCH$_2$CH$_2$Cl	25	48	3 (100 : 0)
2		60	15	quant. (60 : 40)
3		84	0.5	quant. (66 : 34)
4$^{d)}$		84	0.5	62 (92 : 8)
5$^{e)}$		84	0.5	17 (88 : 12)
6$^{f)}$		84	15	92 (92 : 8)
7	ClCH$_3$	61	15	94 (22 : 78)
8	(C$_2$H$_5$)$_2$O	35	15	16 (63 : 37)
9	THF	66	15	trace
10	DMF	85	15	0
11	CH$_3$OH	65	15	trace

a) Reaction conditions: 1a (2 mmol), 2a (6 mmol) and ReBr(CO)$_5$ (0.02 mmol) in solvent (3.5 mL). b) The yields were based on 1a. c) Determined by GC. d) ^{t}BuBr (6 mmol) was used. e) ^{t}BuI (6 mmol) was used. f) ^{t}BuCl (2 mmol) was used.

data obtained for alkylation with t-butyl bromide and iodide for a comparison. The yields of the alkylated products were drastically affected by the solvent used and the reaction temperature. 1,2-Dichloroethane was the most effective solvent for the alkylation of anisole (Entry 3). In chlorinated hydrocarbon solvents, such as chloroform, the introduction of a t-butyl group to anisole also occurred efficiently, whereas the use of coordinating solvents, such as diethyl ether, tetrahydrofuran, dimethylformamide or ethanol, caused a distinct decrease in the yields of 3a and 4a (Entries 7—11). For a reaction at 60 °C, the yields of the alkylated products were improved by a longer reaction time (Entry 2). When t-butyl bromide and iodide were used as the alkyl halide, the yields of the alkylated products were quite low (Entries 4 and 5).

Table 2. Effect of Catalyst on the Alkylation of Anisole (1a) with ^{t}BuCl (2a)[a]

Entry	Catalyst	Time/h	Yield/% (3a : 4a)[b]
1	ReBr(CO)$_5$	0.5	quant. (66 : 34)
2	ReCl(CO)$_5$	0.5	quant. (60 : 40)
3	MnBr(CO)$_5$	15	36 (86 : 14)
4	Re(C$_5$H$_5$)(CO)$_3$	0.5	0
5		15	quant. (78 : 22)
6	Re$_2$(CO)$_{10}$	0.5	0
7		15	91 (82 : 18)
8	MeReO$_3$	15	3 (100 : 0)

a) Reaction condition: 1a (2 mmol), 2a (6 mmol) and catalyst (0.02 mmol) in ClCH$_2$CH$_2$Cl (3.5 mL) at 84 °C. b) Determined by GC.

Table 2 gives the catalytic activity of the other rhenium compounds toward the alkylation of anisole (1a) with t-butyl chloride (2a). The alkylation of 1a with 2a proceeded, even upon using [Re(C$_5$H$_5$)(CO)$_3$] and [Re$_2$(CO)$_{10}$] instead of [ReBr(CO)$_5$] as the catalyst; however, a longer reaction time was required (Entries 5 and 7). The replacement of one of the electron-withdrawing carbonyl ligands by electron-donating phosphines led to a decrease in the yields of the alkylated products (Entry 8). These results indicate that the control of the Lewis acidity of the rhenium complex would be easily achieved by displacing the ligands on the rhenium metal. On the other hand, when an analogous complex of the other element in group 7, [MnBr(CO)$_5$] was employed as the catalyst, the yields of the alkylated products were markedly decreased (Entry 3).

The results of the [ReBr(CO)$_5$]-catalyzed alkylation of anisole with various alkyl chlorides are given in Table 3. 2-Chloro-2-methylbutane could be used as an alkylating reagent (Entry 1). In the case of 2-chlorobutane, a secondary alkyl chloride, a longer reaction time (15 h) led to the formation of alkylated products (Entry 3). During the alkylation of anisole employing the primary alkyl halide, rearranged products were formed (Entry 4).

Table 3. Alkylation of Anisole with Various Alkyl Halides[a]

Entry	RX	Time/h	Yield/% (3 : 4)[b),c)]
1	t-Amyl chloride	0.5	85 (84^d : 16)
2	s-BuCl	0.5	0
3		15	76 (55^e : 14)
4[f)	n-BuCl	15	15 (100^g : 0)

a) Reaction conditions: RCl (6 mmol), anisole (2 mmol) and ReBr(CO)$_5$ (0.02 mmol) in ClCH$_2$CH$_2$Cl (3.5 mL) at 84 °C. b) The yields were based on anisole. c) Determined by GC. d) o:p-isomer = 100:0. e) o:p-isomer = 66:44. f) The reaction was carried out at 120 °C. g) s-Butylanisole (o:p-isomer = 52:48) were formed.

In the presence of a catalytic amount of [ReBr(CO)$_5$] (0.01 equiv), various arenes were allowed to react with t-butyl chloride; these results are given in Table 4. Ethyl phenyl ether showed high reactivity and the mono- and dialkyl substituted arenes were formed in almost quantitative yields (Entry 1). The mono- and dialkyl substituted dimethoxybenzene derivatives were also synthesized by a reaction of the 1, 2-, 1,3- and 1,4-dimethoxybenzenes with t-butyl chloride in moderate-to-good yields (Entries 2-4). The alkylation of phenol with t-BuCl was successfully achieved under the same reaction conditions as that of anisole (Entry 6). In the case of benzene and alkyl benzenes, raising the reaction temperature (120 °C) led to an improvement in the yields of the alkylated benzenes (Entries 8, 10 and 12).[8] In the alkylation of 3-methoxytoluene, 1-t-butyl-2-methyl-4-methoxybenzene, in which the t-butyl group was introduced at the *para* position of the methoxy group, was predominantly formed (Entry 5). When t-BuCl was treated with a mixture of anisole and toluene, the alkylation of anisole proceeded with high selectivity (Eq. 1).
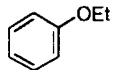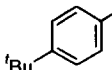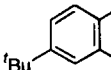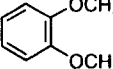

(1)
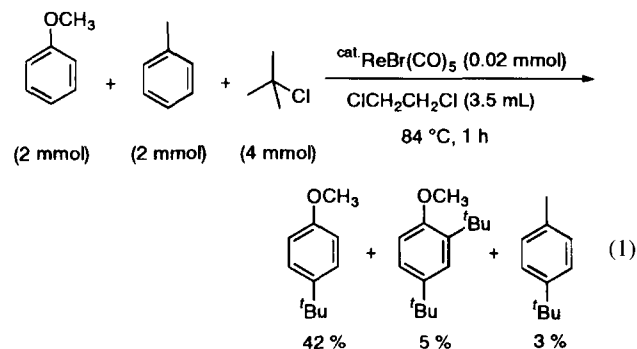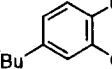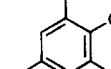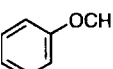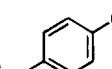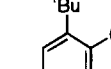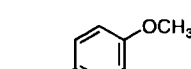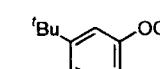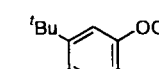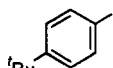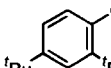
As one of the applications of this rhenium-catalyzed alkylation, we examined the rhenium-catalyzed intramolecular alkylation of arenes. The intramolecular alkylation of 2-bromo-2-methyl-4-(3′-methoxyphenyl)butane, in which one of the hydrogens on the aromatic ring was substituted by a methoxy group, proceeded efficiently to give the corresponding indan in 63% yield with a mixture of isomers; however, the cyclization of 2-bromo-2-methyl-4-phenylbutane was hardly promoted (Eq. 2).

(2)
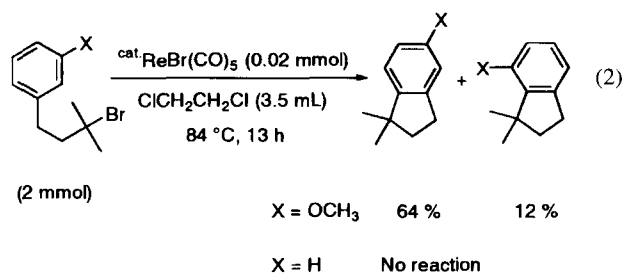
Although we can not show the reaction pathway for the rhenium-catalyzed alkylation of arenes with alkyl halides in detail, we propose the following reaction pathway. It has already been reported that the coordinatively unsaturated 16-electron complex, [ReBr(CO)$_4$], was generated by the dissociation of carbon monoxide from [ReBr(CO)$_5$] under toluene reflux conditions.[9-11] In addition, when the alkylation

Y. Nishiyama et al.

Bull. Chem. Soc. Jpn., 73, No. 12 (2000) 2781

Table 4. ReBr(CO)$_5$-Catalyzed t-Butylation of Various Arenes with ^{t}BuCl[a]

Entry	Arene	Time/h	Product (Yield/%)[b]		
1	OEt (phenetole)	0.5	^{t}Bu–C$_6$H$_4$–OEt (63)		^{t}Bu,^{t}Bu–OEt (35)
2	1,2-(OCH$_3$)$_2$	0.5	^{t}Bu (82)		^{t}Bu, ^{t}Bu, OCH$_3$, OCH$_3$ (10)
3	1,3-(OCH$_3$)$_2$	0.5	(54)		(16)
4	1,4-(OCH$_3$)... H$_3$CO	0.5	(59)		(13)
5	OCH$_3$ (methyl)	5	(93)		
6	OH (phenol)	0.5	(48)		(50)
7[c]	benzene	8	^{t}Bu (15)		(3)
8[c),d]		8	(31)		(12)
9	toluene	15	(33)		(trace)
10[d]		8	(64)		(4)
11	xylene	15	(9)		
12[d]		15	(16)		

a) The reaction was performed using arene (2 mmol), ^{t}BuCl (6 mmol) and ReBr(CO)$_5$ (0.02 mmol) in ClCH$_2$CH$_2$Cl (3.5 mL) at 84 °C. b) Isolated yields. c) Benzene (5 mL) was used. d) At 120 °C.

of anisole with t-BuCl was carried out under the pressure of carbon monoxide, the yields of the alkylated products were dramatically affected by the presence of carbon monoxide 3a (15%) and 4a (12%) under the pressure of CO (30 atm) at 85 °C for 15 h. From these results, we suggest that the first step of the present alkylation is the generation of a 16-electron rhenium species by the dissociation of carbon monoxide from 18-electron rhenium complexes, such as [ReBr(CO)$_5$], [Re(C$_5$H$_5$)(CO)$_3$] or [Re$_2$(CO)$_{10}$]. The reactivity of alkyl halides toward anisole in the presence of rhenium catalyst is consistent with the behavior of the alkyl halides in the presence of other Lewis acid catalysts. Furthermore, the results of formation of rearranged products in alkylation with n-BuCl suggested the generation of carbocation species. From these observations, we suggest that the coordinatively unsaturated rhenium species generated in situ by the liberation of carbon monoxide from the rhenium complex, acts as a Lewis acid, giving the carbocation species.

In summary, we have found that rhenium complexes, such as [ReBr(CO)$_5$], [Re(C$_5$H$_5$)(CO)$_3$] or [Re$_2$(CO)$_{10}$], catalyzed the alkylation of arenes with alkyl halides.

Experimental

General. The ^{1}H- and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-400 (400 and 99.5 MHz) spectrometer using CDCl$_3$ as a solvent with tetramethylsilane as an internal standard. The FT-IR spectra were obtained using a Perkin-Elmer Model PARAGON 1000 spectrophotometer. The mass spectra were measured using a Shimadzu Model QP-5050A. Gas chromatography (GC) was carried out using a Shimadzu GC-14A equipped with a flame ionizing detector with a capillary column (Hicap-CBP-1-S25-025, 0.25 mm×25 m). Layer chromatography was performed using a Merck (60F$_{254}$). Bromopentacarbonyl rhenium(I), tricarbonylcyclopentadienylrhenium(I), decacarbonyldirhenium and bromopentacarbonylmanganese were commercially available as high-grade products and were used without purification. 2-Bromo-2-methyl-4-phenylbutane, 2-bromo-2-methyl-5-phenylpentane and 2-bromo-2-methyl-4-(3′-methoxyphenyl)butane were prepared by bromination of the corresponding alcohols with phos-

phorus tribromide. The other reagents and solvents were purified by the usual methods before use.

General Procedure for the Alkylation of an Arene with an Alkyl Halide in the Presence of a Rhenium Catalyst.   In a 20-mL three-necked glass vessel (or 50 mL stainless steel autoclave) were placed the arene (2 mmol), alkyl halide (6 mmol), bromopentacarbonylrhenium(I) (0.02 mmol, 8 mg) and 1,2-dichloroethane (3.5 mL). The reaction mixture was stirred at 84 °C or 120 °C for 0.5—15h. The reaction mixture was then cooled to room temperature. Evaporation of the solvent and purification by thin-layer chromatography afforded the corresponding alkylated products. The structures of the products were determined by ^{1}H NMR, ^{13}C NMR, IR and GLC mass spectra.

The complete spectral data of the products are deposited as Document No. 73065 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1   For recent reviews, see: a) H. Heaney, in "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford, (1991), Vol. 3, 293. b) R. M. Roberts and A. A. Khalaf, in "Friedel–Crafts Alkylation Chemistry: A Century of Discovery," Dekker, New York (1984). c) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Wiley-Interscience, New York (1963—1965), Vols. 1—4. d) G. A. Olah, Ed.; In Friedel-Crafts Chemistry, Wiley, New York, 1973 and references cited therein.

2   The concept of trasition-metal-based Lewis acid catalysts has been shown by Bosnich et al. The conderlying principle is widely used in the design of new kinds of catalytic reactions.^{3}

3   For recent reviews, see: a) S. I. Murahashi and H. Takaya, *Acc. Chem. Res.*, **23**, 225 (2000); B. Bosnich, *Aldrichimica Acta*, **31**, 76 (1998). b) W. Beck and K. Sunkel, *Chem. Rev.*, **88**, 1405 (1988) and references cited therein.

4   For recent reviews, see: a) W. H. Davenport, V. Kollonitsch, and C. H. Kline, *Ind. Eng. Chem.*, **60**, 10 (1968). b) W. A.

Herrman, in "*Organic Peroxygen Chemistry,*" W. A. Herrman, ed., Springer-Verlag, Belrin (1993) Vol. 164, p. 130. c) H. Kusama, and K. Narasaka, *J. Org. Synth. Chem.*, **54**, 20 (1996) and references cited therein.

5   Recent manuscripts of the catalytic utilization of rhenium compounds: a) J. H. Espenson, *Chem. Commun.*, **1999**, 479. b) S. Komiya, M. Hirano, *Chem. Lett.*, **1999**, 347. c) W. Adam and C. R. Saha-Moller, *J. Am. Chem. Soc.*, **121**, 2097 (1999). d) T. B. Gunnoe and W. D. Harman, *J. Am. Chem. Soc.*, **121**, 6499 (1999). e) J. Jacob and J. H. Espenson, *Chem. Commun.*, **1999**, 1003. f) S. Stankovic and J. H. Espenson, *J. Org. Chem.*, **63**, 4129 (1998). g) Y. Koga, H. Kusama and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **71**, 475 (1998). h) M. S. Gordon and J. H. Espenson, *Organometallics*, **17**, 1835 (1998). i) S. C. Sinha and E. Keinan, *J. Am. Chem. Soc.*, **120**, 9076 (1998). j) H. Rudler and B. Denise, *Chem. Commun.*, **1998**, 2145. k) B. E. Ledford and E. M. Carreira, *Tetrahedron Lett.*, **38**, 8125 (1997). l) Z. Zhu and J. H. Espenson, *Organometallics*, **16**, 3658 (1997). m) J. B. Arterburn and M. C. Perry, *Tetrahedron Lett.*, **37**, 7941 (1996). n) K. N. Brown and J. H. Espenson, *Inorg. Chem.*, **35**, 7211 (1996). o) M. M. Abu-Omar and J. H. Espenson, *Organometallics*, **15**, 3543 (1996). p) Z. Zhu and J. H. Espenson, *J. Org. Chem.*, **61**, 324 (1996). q) J. B. Arterburn and S. L. Nelson, *J. Org. Chem.*, **61**, 2260 (1996). r) U. Volkhardt, R. W. Fischer, M. O. Rauch, and W. Scherer, *J. Mol. Catal.*, **86**, 243 (1994). s) W. A. Herrmann, R. W. Fischer, and D. W. Marz, *Angew. Chem., Int. Ed. Engl.*, **30**, 1638 (1991), Ref. 2b—2c and references cited therein.

6   a) Z. Zhu and J. H. Espenson, *Synthesis*, **1998**, 417. b) H. Kusama and K. Narasaka, *Bull. Chem. Soc. Jpn.*, **68**, 2379 (1995). c) J. Tsuji, T. Nogi, and M. Morikawa, *Bull. Chem. Soc. Jpn.*, **39**, 714 (1966).

7   In 1966, Tsuji reported that ReCl$_5$ could be a catalyst for the alkylation of benzene with alkylhalides. However, the utilization of ReCl$_5$ as a catalyst has, so far, been limited to the alkylation of benzene; see Ref. 4c.

8   Recently, the rhenium complex-catalyzed Friedel–Crafts acylation has been reported.^{5b} However, in the case of the acylation of benzene, the yield was also very low (11%).

9   P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, **1965**, 5259.

10   E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, **1958**, 3149.

11   F. Zingales, U. Sartorelli, F. Canziani, and M. Raveglia, *Inorg. Chem.*, **6**, 154 (1967).