芳基取代四甲基环戊二烯基铼羰基化合物的
合成、晶体结构及催化性能

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摘要：芳基取代的四甲基环戊二烯 C_5HMe_4Ar (Ar=Ph,4-CH₃Ph,4-OCH₃Ph,4-ClPh,4-BrPh) 分别与 $Re_2(CO)_{10}$ 在二甲苯中加热回流,得到了 5 个单核配合物[$(\eta^5-C_5Me_4Ar)Re(CO)_3$](Ar=Ph (**1**),4-CH₃Ph (**2**),4-OCH₃Ph (**3**),4-ClPh (**4**),4-BrPh (**5**))。通过元素分析、红外光谱、核磁共振氢谱对配合物 **1~5** 的结构进行了表征,用 X 射线单晶衍射法测定了配合物的结构。同时,研究了这五种配合物在芳香族化合物 Friedel-Crafts 烷基化反应中的催化活性。

关键词：合成；单核铼羰基配合物；Friedel-Crafts 烷基化反应；催化

Syntheses, Crystal Structures and Catalytic Activity of Rhenium Carbonyl Complexes Containing Aryl-Substituted Tetramethylcyclopentadienyl Ligands

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Abstract: Cyclopentadienes C_5HMe_4Ar (Ar=Ph, 4-CH₃Ph , 4-OCH₃Ph, 4-ClPh, 4-BrPh) reacted with $Re_2(CO)_{10}$ in refluxing xylene to give new aryl-substituted tetramethylcyclopentadienyl mononuclear metal carbonyl complexes [$(\eta^5-C_5Me_4Ar)Re(CO)_3$] (Ar=Ph (**1**), 4-CH₃Ph (**2**), 4-OCH₃Ph (**3**), 4-ClPh (**4**), 4-BrPh (**5**)), respectively. The five new complexes were characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy. The crystal structures of complexes **1~5** were determined by X-ray crystal diffraction analysis. All five of these complexes have significant catalytic activity in Friedel-Crafts reactions of aromatic compounds with alkylation reagents. CCDC: 1463217, **1**; 1506704, **2**; 1484954, **3**; 1484955, **4**; 1506705, **5**.

Keywords: synthesis; mononuclear rhenium carbonyl complex; Friedel-Crafts alkylation reaction; catalysis

0 Introduction

Cyclopentadienyl ligands have been studied intensively as the most important ligands in organometallic chemistry because of their capacity for binding to hard and soft metal centers in a hemilabile manner, giving the complexes distinctive chemical and physical properties. Substituents on such ligands may include phosphines[1-2], amines[3-4], ethers[5-8], sulfids[9-11] and alkenes[12-16], which have been widely studied. These types of complexes have been significantly applied in catalysis and in the construction of molecular materials. Despite these notable contributions, the development of functionalized ligands bearing other substituents remains a worthwhile task. Our group has reported a series of substituted cyclopentadienyl metal carbonyl complexes, and the electronic and steric effects of the substituents on the final structures and properties of the complexes were discussed[17-19]. We have also reported catalytic reactivity of mononuclear substituted tetramethylcyclopentadienyl molybdenum carbonyl complexes in Friedel-Crafts alkylation of aromatic compounds[20]. However, few half-sandwich complexes of this type are known for rhenium[21-23]. On the other hand, to the best of our knowledge, only a few examples of Friedel-Crafts alkylation reactions catalyzed by rhenium carbonyl complexes have been reported to date[24-25]. To develop a deeper understanding of the structures and catalytic activity of substituted cyclopentadienyl rhenium carbonyl complexes, herein we report the syntheses, structures and catalytic activity of a series of aryl-substituted tetramethylcyclopentadienyl rhenium carbonyl complexes.

1 Experimental

1.1 General considerations

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av Ⅲ-500 instrument in CDCl$_3$. IR spectra were recorded as KBr disks on a Thermo Fisher is 50 spectrometer. Agilent 6820 gas chromatograms were used for analysis of samples. Elemental analyses were obtained on a Vario EL Ⅲ analyzer. The ligand precursors C$_5$HMe$_4$Ar (Ar=Ph, 4-CH$_3$Ph, 4-OCH$_3$Ph, 4-ClPh, 4-BrPh) were synthesized according to the literature[26-27]. Treatment of ligand precursors (C$_5$HMe$_4$Ar) with Re$_2$(CO)$_{10}$ afforded the corresponding complexes [(η^5-C$_5$Me$_4$Ar)Re(CO)$_3$] (Ar =Ph (**1**), 4-CH$_3$Ph (**2**), 4-OCH$_3$Ph (**3**), 4-ClPh (**4**), 4-BrPh (**5**)) (Scheme 1).
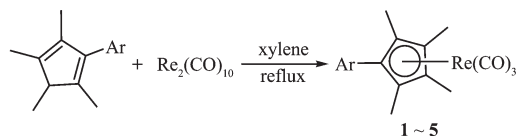
Ar=Ph (**1**), 4-CH$_3$Ph (**2**), 4-OCH$_3$Ph (**3**), 4-ClPh (**4**), 4-BrPh (**5**)

Scheme 1 Syntheses of complexes **1~5**

1.2 Synthesis of complex 1

A solution of the ligand (C$_5$HMe$_4$Ph) (0.12 g, 0.6 mmol) and Re$_2$(CO)$_{10}$ (0.2 g, 0.3 mmol) in xylene (15 mL) was refluxed for 48 h. After removal of solvent the residue was loaded onto an alumina column. Elution with petroleum ether developed a colorless band, which was collected and concentrated to afford (η^5-C$_5$Me$_4$Ph)Re(CO)$_3$ (**1**) as colorless crystals, yield: 0.19 g (67.4%). m.p. 128.3~128.9 ℃; Anal. Calcd. for C$_{18}$H$_{17}$O$_3$Re(%): C, 46.24; H, 3.66. Found(%): C, 45.87; H, 3.87; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 2.11 (s, 6H, C$_5$Me$_2$), 2.24 (s, 6H, C$_5$Me$_2$), 7.29~7.38 (m, 5H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 10.85, 11.24, 97.53, 102.11, 105.03, 127.75, 128.43, 132.11, 132.64, 197.45; IR(KBr, cm^{-1}): 2 006(s), 1 931(s), 1 900(s).

1.3 Synthesis of complex 2

Using a procedure similar to that described above, C$_5$HMe$_4$(4-CH$_3$Ph) was reacted with Re$_2$(CO)$_{10}$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, [η^5-C$_5$Me$_4$(4-CH$_3$Ph)]Re(CO)$_3$ (**2**) was obtained (0.23 g, 76.7% yield) as colorless crystals. m.p. 127.0~127.5℃; Anal. Calcd. for C$_{19}$H$_{19}$O$_3$Re(%): C, 47.39; H, 3.98. Found(%): C, 47.58; H, 3.81; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 2.11 (s, 6H, C$_5$Me$_2$), 2.23 (s, 6H, C$_5$Me$_2$), 2.38 (s, 3H, CH$_3$), 7.18 (s, 4H, C$_6$H$_4$); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 10.85, 11.25, 21.14, 97.49, 102.01, 105.01, 129.01, 129.12, 132.46, 137.55, 197.55. IR(KBr, cm^{-1}): 2 004(s), 1 923(s), 1 899(s).

1.4　Synthesis of complex 3

Using a procedure similar to that described above, $C_5HMe_4(4-OCH_3Ph)$ was reacted with $Re_2(CO)_{10}$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, $[\eta^5-C_5Me_4(4-OCH_3Ph)]$ $Re(CO)_3$ (**3**) was obtained (0.19 g, 61.9% yield) as colorless crystals. m.p. 119.8~120.6 ℃; Anal. Calcd. for $C_{19}H_{19}O_4Re(\%)$: C, 45.87; H, 3.85. Found(%): C, 45.54; H, 3.74; ^1H NMR (CDCl$_3$, 500 MHz): δ 2.10 (s, 6H, C_5Me_2), 2.23 (s, 6H, C_5Me_2), 3.84 (s, 3H, CH_3), 6.89 (d, J=8.5 Hz, 2H, C_6H_2), 7.21 (d, J=8.0 Hz, 2H, C_6H_2); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 10.86, 11.25, 55.31, 97.43, 102.16, 104.81, 113.77, 124.10, 133.70, 159.12 197.60. IR (KBr, cm^{-1}): 2 005(s), 1 918(s), 1 903(s).

1.5　Synthesis of complex 4

Using a procedure similar to that described above, $C_5HMe_4(4-ClPh)$ was reacted with $Re_2(CO)_{10}$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, $[\eta^5-C_5Me_4(4-ClPh)]Re$ $(CO)_3$ (**4**) was obtained (0.23 g, 73.5% yield) as colorless crystals. m.p. 137.8 ~138.0 ℃; Anal. Calcd. for $C_{18}H_{16}ClO_3Re(\%)$: C, 43.07; H, 3.21. Found(%): C, 43.38; H, 3.02; ^1H NMR (CDCl$_3$, 500 MHz): δ 2.10 (s, 6H, C_5Me_2), 2.23 (s, 6H, C_5Me_2), 7.24 (d, J=8.0 Hz, 2H, C_6H_2), 7.34 (d, J=8.5 Hz, 2H, C_6H_2); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 10.85, 11.24, 97.54, 102.11, 105.04, 127.75, 128.43, 132.12, 132.54, 197.46. IR (KBr, cm^{-1}): 2 005(s), 1 922(s), 1 897(s).

1.6　Synthesis of complex 5

Using a procedure similar to that described above, $C_5HMe_4(4-BrPh)$ was reacted with $Re_2(CO)_{10}$ in refluxing xylene for 48 h. After chromatography and elution with petroleum ether, $[\eta^5-C_5Me_4(4-BrPh)]Re$ $(CO)_3$ (**5**) was obtained (0.21 g, 63.6% yield) as colorless crystals. m.p. 115.0~116.0 ℃; Anal. Calcd. for $C_{18}H_{16}BrO_3Re(\%)$: C, 39.56; H, 2.95. Found(%): C, 39.93; H, 3.12; ^1H NMR (CDCl$_3$, 500 MHz): δ 2.10 (s, 6H, C_5Me_2), 2.23 (s, 6H, C_5Me_2), 7.17 (d, J=8.0 Hz, 2H, C_6H_2), 7.50 (d, J=8.5 Hz, 2H, C_6H_2). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 10.83, 11.21, 97.79, 102.01, 103.50, 121.96, 131.25, 131.62, 134.18, 197.10. IR(KBr, cm^{-1}): 2 005 (s), 1 920(s), 1 900(s).

1.7　Crystallographic characterization

Single crystals of complexes **1~5** suitable for X-ray diffraction were obtained from the slow evaporation of hexane-dichloromethane solutions. All X-ray crystallographic data were collected on a Bruker AXS SMART 1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation using the φ-ω scan technique. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELXL -97 program system[28]. Hydrogen atoms were included in calculated positions riding on the parent atoms and refined with fixed thermal parameters. The crystal data and summary of X-ray data collection are presented in Table 1.

CCDC: 1463217, **1**; 1506704, **2**; 1484954, **3**; 1484955, **4**; 1506705, **5**.

1.8　General procedure for catalytic tests

The catalytic reactions were carried out under an

Table 1　Crystal data and structure refinement parameters for complexes 1~5

Complex	1	2	3	4	5
Empirical formula	$C_{18}H_{17}O_3Re$	$C_{19}H_{19}O_3Re$	$C_{19}H_{19}O_4Re$	$C_{18}H_{16}ClO_3Re$	$C_{18}H_{16}BrO_3Re$
Formula weight	467.52	481.54	497.54	501.96	546.42
Temperature / K	298(2)	298(2)	293(2)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pbca$	$P2_1/n$	C_2	$P2_1/c$	$P2_1/c$
a / nm	1.509 43(13)	1.195 56	1.464 78	1.587 82(13)	1.603 19(16)
b / nm	1.220 34(11)	0.973 09(9)	0.787 79(7)	0.758 47(6)	0.764 55(7)
c / nm	1.809 63(15)	1.625 85(14)	1.638 71(14)	1.449 88(12)	1.459 84(13)
β / (°)	90	111.262(2)	97.136 0(10)	97.102 0(10)	97.742 0(10)
Volume / nm^3	3.333 4(5)	1.762 7(3)	1.876 3(3)	1.732 7(2)	1.773 0(3)

Continued Table 1

Z	8	4	4	4	4
D_c / (g·cm^{-3})	1.863	1.814	1.761	1.924	2.047
μ / mm^{-1}	7.300	6.905	6.494	7.178	9.118
$F(000)$	1 792	928	960	960	1 032
Crystal size / mm	0.35×0.24×0.17	0.42×0.37×0.36	0.45×0.40×0.33	0.40×0.38×0.21	0.40×0.34×033
θ range / (°)	2.42~25.02	2.49~5.02	2.51~5.03	2.83~5.02	2.56~5.02
Reflections collected, Unique	15 755, 2 933	8 543, 3 120	4 130, 2 909	7 643, 2 970	8 643, 3 101
Rint	0.064 4	0.034 1	0.104 5	0.119 5	0.141 7
Completeness to θ / %	99.90	99.90	97.80	97.60	99.30
Max. and min. transmission	0.370 0 and 0.184 4	0.190 1 and 0.159 5	0.230 4 and 0.158 1	0.314 1 and 0.161 4	0.152 8 and 0.121 4
Data, restraints, parameters	2 933, 0, 199	3 120, 0, 208	2 909, 1, 223	2 970, 0, 212	3 101, 0, 212
Goodness-of-fit on F^2	1.052	1.075	1.054	1.11	1.085
R_1, wR_2 [$I>2\sigma(I)$]	0.032 2, 0.062 0	0.024 8, 0.058 5	0.145 2, 0.315 2	0.081 4, 0.186 3	0.077 4, 0.191 1
R_1, wR_2 (all data)	0.080 4, 0.076 6	0.034 7, 0.062 0	0.167 4, 0.328 9	0.109 7, 0.198 8	0.095 5, 0.204 8
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	907, −955	555, −1 263	7 007, −7 667	4 452, −6 853	3 801, −4 736

argon atmosphere with magnetic stirring. The required rhenium carbonyl complex (0.04 mmol) was mixed with 1,2-dichloroethane (3.5 mL) in a 25 mL round-bottom flask at room temperature. Aromatic compounds (2 mmol) and *tert*-butyl halides (4 mmol) were added by syringe. The reaction mixture was stirred at 80 ℃ for 18 h. After cooling to room temperature, the solid catalyst was separated from the reaction mixture by filtration. The filtrate was concentrated by rotary evaporation, and the residue was purified by Al_2O_3 column chromatography, eluting with petroleum ether to give a colorless liquid. The course of the reaction was monitored using an Agilent 6820 gas chromatograph.

2　Results and discussion

2.1　Crystal structures

　　The selected bond distances and angles for complexes **1~5** are presented in Table 2 and complex **1** is depicted in Fig.1. The four remaining complexes [(η^5-C$_5$Me$_4$Ar)Re (CO)$_3$] (Ar =4-CH$_3$Ph (**2**), 4-OCH$_3$Ph (**3**), 4-ClPh (**4**), 4-BrPh (**5**)) are shown in Fig.S1~S4 (Supporting Information).

　　Complexes **1~5** are mononuclear substituted tetramethylcyclopentadienyl rhenium carbonyl complexes and have similar structures. Similar to the CpRe(CO)$_3$ type (Cp=substituted cyclopentadienyl ligand), all five structures exhibit typical three-legged piano-stool structures, in which the rhenium atom is coordinated by a η^5-cyclopentadienyl, plus three terminal CO ligands. The Re-CEN (CEN: centroid of the cyclopentadienyl ring) distances are 0.195 1 nm for **1**, 0.196 2 nm for **2**, 0.203 8 nm for **3**, 0.194 2 nm for **4**, and 0.195 3 nm for **5**, which are correlated with the steric effects of the different cyclopentadienyl substituents. The (O)C-Re-C(O) angle in all of these Re tricarbonyl complexes investigated is very close to 90°, which
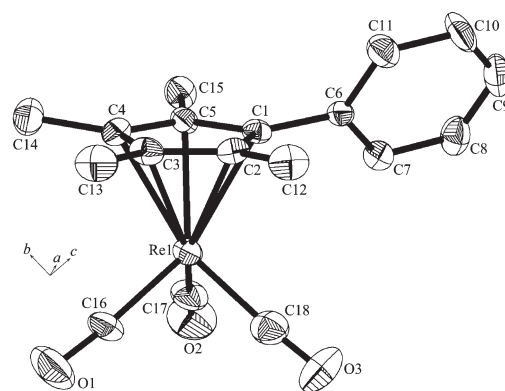
Ellipsoids probability: 30%; Hydrogen atoms are omitted for clarity

Fig.1　Molecular structure of complex **1**

Table 2　Selected bond lengths (nm) and angles (°) for complexes 1~5

1					
C(1)-C(2)	0.146 0(10)	C(3)-C(4)	0.146 1(11)	Re(1)-C(17)	0.190 5(9)
C(1)-C(5)	0.142 9(9)	C(4)-C(5)	0.141 3(10)	Re(1)-C(18)	0.190 9(11)
C(2)-C(3)	0.142 5(10)	Re(1)-C(16)	0.188 8(9)	Re(1)-CEN	0.195 1
C(16)-Re(1)-C(17)	91.0(4)	O(1)-C(16)-Re(1)	175.3(8)	Cp-Ar	61.86
C(16)-Re(1)-C(18)	90.7(4)	O(2)-C(17)-Re(1)	177.0(8)		
C(17)-Re(1)-C(18)	89.4(4)	O(3)-C(18)-Re(1)	176.1(9)		
2					
C(1)-C(2)	0.145 5(6)	C(3)-C(4)	0.144 3(7)	Re(1)-C(18)	0.191 4(6)
C(1)-C(5)	0.143 8(7)	C(4)-C(5)	0.143 5(6)	Re(1)-C(19)	0.192 7(6)
C(2)-C(3)	0.141 8(7)	Re(1)-C(17)	0.189 9(6)	Re(1)-CEN	0.196 2
C(17)-Re(1)-C(18)	89.7(2)	O(1)-C(17)-Re(1)	175.6(5)	Cp-Ar	59.9
C(17)-Re(1)-C(19)	91.4(2)	O(2)-C(18)-Re(1)	178.0(5)		
C(18)-Re(1)-C(19)	88.8(2)	O(3)-C(19)-Re(1)	177.0(5)		
3					
C(1)-C(2)	0.146(8)	C(3)-C(4)	0.141(7)	Re(1)-C(18)	0.200(5)
C(1)-C(5)	0.138(9)	C(4)-C(5)	0.145(6)	Re(1)-C(19)	0.192(4)
C(2)-C(3)	0.144(7)	Re(1)-C(17)	0.190(7)	Re(1)-CEN	0.203 8
C(17)-Re(1)-C(18)	92(3)	O(2)-C(17)-Re(1)	173(5)	Cp-Ar	57.56
C(17)-Re(1)-C(19)	90(2)	O(3)-C(18)-Re(1)	175(4)		
C(18)-Re(1)-C(19)	92.2(18)	O(4)-C(19)-Re(1)	175(4)		
4					
C(1)-C(2)	0.141(2)	C(3)-C(4)	0.145(2)	Re(1)-C(17)	0.193 3(18)
C(1)-C(5)	0.145(2)	C(4)-C(5)	0.142(2)	Re(1)-C(18)	0.189 6(16)
C(2)-C(3)	0.145(2)	Re(1)-C(16)	0.185 1(19)	Re(1)-CEN	0.194 2
C(16)-Re(1)-C(17)	89.7(7)	O(1)-C(16)-Re(1)	176.9(18)	Cp-Ar	56.03
C(16)-Re(1)-C(18)	92.5(8)	O(2)-C(17)-Re(1)	175.2(17)		
C(17)-Re(1)-C(18)	90.4(8)	O(3)-C(18)-Re(1)	174.0(17)		
5					
C(1)-C(2)	0.145 7(18)	C(3)-C(4)	0.141(2)	Re(1)-C(17)	0.194 8(15)
C(1)-C(5)	0.145 4(16)	C(4)-C(5)	0.143 2(18)	Re(1)-C(18)	0.191 5(17)
C(2)-C(3)	0.143(2)	Re(1)-C(16)	0.194 5(19)	Re(1)-CEN	0.195 3
C(16)-Re(1)-C(17)	87.8(6)	O(1)-C(16)-Re(1)	175.5(15)	Cp-Ar	56.58
C(16)-Re(1)-C(18)	93.2(8)	O(2)-C(17)-Re(1)	173.8(16)		
C(17)-Re(1)-C(18)	88.3(7)	O(3)-C(18)-Re(1)	174.6(15)		

CEN: centroid of the cyclopentadienyl ring; Cp: plane of cyclopentadienyl; Ar: plane of benzene

may simply be a consequence of the reduction in non-bonded repulsions between carbonyl groups. The dihedral angles between the cyclopentadienyl and phenyl ring planes in these complexes are between 56.03° and 61.86°, to further decrease the intramolecular non-bonding interaction. On the other hand, the average Re-C(O) distances and the Re-C-O angles of the five complexes are concordant with related

tricarbonyl cyclopentadienyl rhenium(I) complexes[29-30].

2.2　Catalytic studies

In order to test the catalytic capability in Friedel-Crafts alkylation reactions (Scheme 2) catalyzed by these complexes, the effects of the reaction time, yield, economic considerations etc. were considered. The experimental conditions were chosen for catalytic work: 1,2-dichloroethane as solvent; the molar ratio of aromatic substrates and alkylation reagents was 1:2; the amount of catalyst was 2% (molar percentage, substrate as reference); refluxing temperature; reaction time: 18 h.

R=OCH$_3$ (**6**), OH (**7**); X=Br, Cl
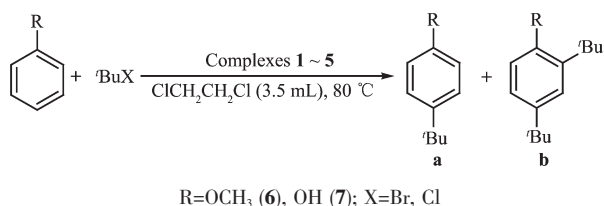
Scheme 2　$[(\eta^5\text{-}C_5Me_4Ar)Re(CO)_3]$ catalyzed Friedel-Crafts alkylation reaction of anisole/phenol with *tert*-butyl bromide/chloride

Complexes **1~5** were examined under the experimental conditions, with the results shown in Table 3. Using refluxing 1,2-dichloroethane, mixtures of the corresponding mono- and di-substituted products were obtained. All five complexes proved to be capable of catalyzing Friedel-Crafts alkylation reactions, moreover, the product yields were found to vary with the different catalysts used. In no case there was any detectable alkylation product in the absence of the rhenium complexes. The obvious influence of the different substituents on the catalytic behavior may be due to their modest variations in steric and electronic properties. The higher product yields obtained for the

Table 3　Complexes catalyzed reaction of aromatic substrates with different alkylation reagents

Complex	Yield of Anisole (w_a / w_b) / %		Yield of Phenol (w_a / w_b) / %	
	^tBuBr	^tBuCl	^tBuBr	^tBuCl
1	45.4(60:40)	2.1(100:0)	80.4(0:100)	5.1(0:100)
2	14.8(100:0)	11.2(100:0)	62.1(10:90)	9.1(91:8)
3	74.1(63:36)	59.6(100:0)	87.7(39:61)	trace
4	55.9(37:63)	22.2(100:0)	69.5(34:67)	trace
5	40.7(39:61)	32.7(48:52)	79.8(5:95)	4.6(0:100)

alkylation of anisole and phenol with *t*-butyl bromide than with *t*-butyl chloride is expected, since bromide is a better leaving group.

3　Conclusions

Reactions of aryl-substituted tetramethylcyclopentadienyl ligands C_5HMe_4Ar (Ar=Ph, 4-CH$_3$Ph, 4-OCH$_3$Ph, 4-ClPh, 4-BrPh) with Re$_2$(CO)$_{10}$ in refluxing xylene furnished five new mononuclear rhenium carbonyl complexes. Friedel-Crafts reactions of aromatic substrates with *tert*-butyl halides catalyzed by these complexes showed that they have obvious catalytic activity. *tert*-Butyl halides could be used as alkylation reagents in these reactions. Compared with traditional catalysts, these complexes have some significant practical advantages, namely lower amounts of catalyst, mild reaction conditions, and more environmentally friendly chemistry. Further studies to elucidate the reaction mechanism and expand the synthetic utility of these catalysts are in progress.

Supporting information is available at http://www.wjhxxb.cn

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