



Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

# Syntheses, structures and catalytic activity for Friedel-Crafts reactions of substituted indenyl rhenium carbonyl complexes

Zhihong Ma, Xinli Zhang, Hong Wang, Zhangang Han, Xuezhong Zheng & Jin Lin

To cite this article: Zhihong Ma, Xinli Zhang, Hong Wang, Zhangang Han, Xuezhong Zheng & Jin Lin (2017) Syntheses, structures and catalytic activity for Friedel-Crafts reactions of substituted indenyl rhenium carbonyl complexes, Journal of Coordination Chemistry, 70:4, 709-721, DOI: 10.1080/00958972.2016.1276573

To link to this article: http://dx.doi.org/10.1080/00958972.2016.1276573



View supplementary material 🕝

đ	1	ſ	L
F	H	F	Η
E			۲

Accepted author version posted online: 23 Dec 2016. Published online: 06 Jan 2017.



🕼 Submit your article to this journal 🗗

Article views: 11



💽 View related articles 🗹



View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gcoo20



# Syntheses, structures and catalytic activity for Friedel-Crafts reactions of substituted indenyl rhenium carbonyl complexes

Zhihong Ma<sup>a</sup>, Xinli Zhang<sup>b</sup>, Hong Wang<sup>c</sup>, Zhangang Han<sup>b</sup>, Xuezhong Zheng<sup>b</sup> and Jin Lin<sup>b</sup>

<sup>a</sup>College of Basic Medicine, Hebei Medical University, Shijiazhuang, PR China; <sup>b</sup>The College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang, PR China; <sup>c</sup>Hebei Institute of Food Quality Supervision Inspection and Research, Shijiazhuang, PR China

#### ABSTRACT

The complexes  $[(\eta^{5}-C_{9}H_{6}R)Re(CO)_{3}]$  [R = "Bu (8), 'Bu (9), CH(CH<sub>2</sub>)<sub>4</sub> (10), Ph (11), Bz (12), 4-methoxyphenyl (13), 4-chlorophenyl (14)] were synthesized by refluxing substituted indenyl ligands  $[C_{9}H_{7}R]$ [R = "Bu (1), 'Bu (2), CH(CH<sub>2</sub>)<sub>4</sub> (3), Ph (4), Bz (5), 4-methoxyphenyl (6), 4-chlorophenyl (7)], and Re<sub>2</sub>(CO)<sub>10</sub> in decalin. The molecular structures of 9, 10, 12, and 13 were determined by X-ray diffraction analysis. These four crystals have similar molecular structures of the mononuclear carbonyl complex. In each of these molecules, Re is  $\eta^{5}$ -coordinated to the five-membered ring of the indenyl group. Complexes 8–14 have catalytic activity for Friedel-Crafts reactions of aromatic compounds with a variety of alkylation and acylation reagents. Compared with traditional catalysts, these mononuclear metal carbonyl complexes have obvious advantages such as high activities, mild reaction conditions, high selectivity, and environmentally friendly chemistry.

#### **ARTICLE HISTORY**

Received 10 March 2016 Accepted 8 November 2016

#### **KEYWORDS**

Synthesis; mononuclear rhenium carbonyl complex; indenyl; Friedel-Crafts reaction



CONTACT Zhihong Ma 🐼 mazhihong-1973@163.com; Jin Lin 🐼 linjin@hebtu.edu.cn

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/00958972.2016.1276573.

710 😔 Z. MA ET AL.

#### 1. Introduction

Transition metal complexes containing indenyl have various metal-indenyl bonding modes, enhanced reactivity, and catalytic ability as compared with the cyclopentadienyl analogs [1–10]. Steric and electronic effects of indenyl ring substituents greatly influence catalytic activity and stability of the substituted indenyl complexes [5]. Thus, variation of indenyl ligands is the first strategy for efficient catalysts. In previous work, we studied reactions of substituted indenes with  $Ru_3(CO)_{12}$  and obtained a series of dinuclear and trinuclear ruthenium carbonyl complexes involving intramolecular C–H activation [11–13]. These substituents with special electronic and steric effect on the complexes have important effects on the physicochemical properties of the complexes [14–18]. To explore the relationship between structure and reactivity of the substituents in indenyl metal complexes, a series of substituted indenyl rhenium carbonyl complexes was synthesized and characterized. Their catalytic reactivity for Friedel-Crafts alkylation and acylation was also studied.

#### 2. Experimental

#### 2.1. General considerations

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 500 instrument in  $CDCl_3$ , while IR spectra were recorded as KBr disks on an IR FT 8900 spectrometer. Agilent 6820 gas chromatograms were recorded for analysis of samples. The ligand precursors  $[C_9H_7R]$   $[R = {}^nBu$  (1),  ${}^tBu$  (2),  $CH(CH_2)_4$  (3), Ph (4), Bz (5), 4-methoxyphenyl (6), 4-chlorophenyl (7)] were synthesized according to the literature [19–25].

#### 2.2. Synthesis of 8

A solution of **1** (0.106 g, 0.614 mmol) and Re<sub>2</sub>(CO)<sub>10</sub> (0.2 g, 0.307 mmol) in decalin (6 mL) was refluxed for 24 h. After removal of solvent, the residue was loaded on an alumina column. After elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (6:1), a yellow band was collected and concentrated. [( $\eta^{5}$ -C<sub>9</sub>H<sub>6</sub><sup>n</sup>Bu)Re(CO)<sub>3</sub>] (**8**) was afforded as a yellow solid; yield: 0.194 g (71.6%). M.p. 92 °C. Anal. Calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub>Re: C, 43.53; H, 3.42. Found (%): C, 43.50; H, 3.39; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  0.99 (t, 3H, *J* = 7.0 Hz, CH<sub>3</sub>), 1.42–1.67 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>), 2.68–2.95 (m, 2H, C<sub>9</sub>H<sub>6</sub>CH<sub>2</sub>), 5.62 (s, 2H, C<sub>9</sub>H<sub>6</sub>), 7.08–7.13 (m, 2H, C<sub>9</sub>H<sub>6</sub>), 7.46 (d, 1H, *J* = 7.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.56 (d, 1H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  13.9, 22.6, 26.6, 34.2, 67.6, 90.7, 95.3, 106.7, 108.0, 122.5, 123.5, 125.4, 126.3, 194.1; IR ( $v_{cor}$  cm<sup>-1</sup>): 2015(s), 1950(s).

#### 2.3. Synthesis of 9

Using a procedure similar to that described above, **2** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^5$ -C<sub>9</sub>H<sub>6</sub>'Bu) Re(CO)<sub>3</sub>] (**9**) was obtained (0.175 g, 64.6% yield) as yellow crystals. M.p.: 90 °C; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub>Re: C, 43.53; H, 3.42. Found (%): C, 43.57; H, 3.44; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  1.49 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>), 5.63 (d, 2H, *J* = 6.5 Hz, C<sub>9</sub>H<sub>6</sub>), 7.02 (t, 1H, *J* = 7.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.12 (t, 1H, *J* = 8.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.49 (d, 1H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>), 7.74 (d, 1H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):

δ 32.4, 32.5, 68.1, 90.7, 105.5, 106.8, 107.6, 123.3, 124.8, 125.2, 126.1, 194.0; IR ( $v_{co'}$  cm<sup>-1</sup>): 2009(s), 1896(s).

#### 2.4. Synthesis of 10

Using a procedure similar to that described above, **3** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^{5-C_9}H_6CH(CH_2)_4$ )Re(CO)<sub>3</sub>] (**10**) was obtained (0.210 g, 75.5% yield) as yellow crystals. M.p.: 80 °C; Anal. Calcd for C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>Re: C, 45.02; H, 3.33. Found (%): C, 45.12; H, 3.23; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  1.38–2.17 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 3.29 (t, 1H, *J* = 8.0 Hz, CH), 5.59 (d, 2H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>), 7.04–7.11 (m, 2H, C<sub>9</sub>H<sub>6</sub>), 7.44 (d, 1H, *J* = 8.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.57 (d, 1H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  25.3, 25.8, 34.9, 35.7, 37.6, 67.7, 89.3, 99.4, 107.2, 107.7, 122.6, 123.7, 125.5, 126.1, 194.1; IR ( $\nu_{co'}$  cm<sup>-1</sup>): 2015(s), 1919(s).

#### 2.5. Synthesis of 11

Using a procedure similar to that described above, **4** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^5$ -C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>5</sub>)Re(CO)<sub>3</sub>] (**11**) was obtained (0.194 g, 68.6% yield) as yellow solid. M.p.: 94 °C; Anal. Calcd for C<sub>18</sub>H<sub>11</sub>O<sub>3</sub>Re: C, 46.85; H, 2.40. Found (%): C, 46.87; H, 2.52; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.77 (d, 1H, *J* = 3.0 Hz, C<sub>9</sub>H<sub>6</sub>), 5.95 (d, 1H, *J* = 3.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.11–7.18 (m, 2H, C<sub>9</sub>H<sub>6</sub>Ph), 7.36 (t, 1H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>Ph), 7.43 (t, 2H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>Ph), 7.52 (d, 1H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>Ph), 7.60 (d, 2H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>Ph), 7.76 (d, 1H, *J* = 8.0 Hz, C<sub>9</sub>H<sub>6</sub>Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  69.5, 91.8, 95.2, 106.9, 107.3, 122.4, 124.0, 126.3, 126.5, 128.0, 128.9, 129.6, 133.3, 193.5; IR ( $v_{co}$ , cm<sup>-1</sup>): 2011(s), 1919(s).

#### 2.6. Synthesis of 12

Using a procedure similar to that described above, **5** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^{5-C_9}H_6CH_2C_6H_5$ )Re(CO)<sub>3</sub>] (**12**) was obtained (0.189 g, 64.7% yield) as yellow crystals. M.p.: 144 °C; Anal. Calcd for C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>Re: C, 47.99; H, 2.76. Found (%): C, 47.83; H, 2.67; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  4.14 (dd, 2H, *J* = 89.5, 15.5 Hz, CH<sub>2</sub>), 5.45 (d, 1H, *J* = 2.5 Hz, C<sub>9</sub>H<sub>6</sub>), 5.59 (d, 1H, *J* = 2.5 Hz, C<sub>9</sub>H<sub>6</sub>), 7.07–7.13 (m, 2H, CH<sub>2</sub>), 7.23–7.34 (m, 5H, C<sub>9</sub>H<sub>6</sub>CH<sub>2</sub>Ph), 7.45 (d, 1H, *J* = 7.5 Hz, C<sub>9</sub>H<sub>6</sub>CH<sub>2</sub>Ph), 7.59 (d, 1H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>CH<sub>2</sub>Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  33.2, 68.0, 91.8, 93.7, 107.1, 108.2, 122.2, 125.8, 126.4, 126.9, 128.6, 128.7, 139.3, 193.7; IR ( $v_{CO}$ , cm<sup>-1</sup>): 2017(s), 1903(s).

#### 2.7. Synthesis of 13

Using a procedure similar to that described above, **6** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^5$ -C<sub>9</sub>H- $_6$ C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>)Re(CO)<sub>3</sub>] (**13**) was obtained (0.151 g, 50.0% yield) as yellow crystals. M.p.: 105 °C; Anal. Calcd for C<sub>19</sub>H<sub>13</sub>O<sub>4</sub>Re: C, 46.43; H, 2.67. Found (%): C, 46.52; H, 2.56; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  3.86 (s, 3H, OCH<sub>3</sub>), 5.74 (d, 1H, *J* = 2.5 Hz, C<sub>9</sub>H<sub>6</sub>), 5.89 (d, 1H, *J* = 2.5 Hz, C<sub>9</sub>H<sub>6</sub>), 6.96 (d, 2H, *J* = 9.0 Hz, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>), 7.09–7.16 (m, 2H, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>), 7.51 (t, 3H, *J* = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>),

#### 712 😔 Z. MA ET AL.

7.72 (d, 1H, J = 8.5 Hz,  $C_9H_6C_6H_4$ ); <sup>13</sup>C NMR (CDCI<sub>3</sub>, 125 MHz):  $\delta$  55.4, 69.0, 91.6, 95.5, 106.8, 107.2, 114.3, 122.5, 123.9, 125.3, 126.2, 126.3, 130.9, 159.4, 193.7; IR ( $v_{CO}$ , cm<sup>-1</sup>): 2011(s), 1909(s).

#### 2.8. Synthesis of 14

Using a procedure similar to that described above, **7** reacted with  $\text{Re}_2(\text{CO})_{10}$  in refluxing decalin for 24 h; after chromatography and elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, [( $\eta^5$ -C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>Cl)Re(CO)<sub>3</sub>] (**14**) was obtained (0.132 g, 43.4% yield) as yellow solid. M.p.: 110 °C; Anal. Calcd for C<sub>18</sub>H<sub>10</sub>O<sub>3</sub>ClRe: C, 43.59; H, 2.03. Found (%): C, 43.72; H, 2.12; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.78 (d, 1H, J = 2.5 Hz, C<sub>9</sub>H<sub>6</sub>), 5.93 (d, 1H, J = 3.0 Hz, C<sub>9</sub>H<sub>6</sub>), 7.12–7.20 (m, 2H, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>), 7.40 (d, 2H, J = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>), 7.52–7.55 (m, 3H, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>), 7.71 (d, 1H, J = 8.5 Hz, C<sub>9</sub>H<sub>6</sub>C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  69.8, 91.8, 93.6, 106.9, 107.2, 122.0, 124.1, 126.4, 126.8, 129.1, 130.8, 132.0, 133.8, 193.2; IR ( $v_{CO}$ , cm<sup>-1</sup>): 2013(s), 1909(s).

#### 2.9. Crystallographic studies

Single crystals of **9**, **10**, **12**, and **13** suitable for X-ray diffraction were obtained from slow evaporation of hexane-dichloromethane solutions. All X-ray crystallographic data were collected on a Bruker Smart APEX diffractometer with graphite monochromated Mo Ka

Complex	9	10	12	13
Empirical formula	C <sub>16</sub> H <sub>16</sub> O <sub>2</sub> Re	C,,H,,O,Re	C <sub>10</sub> H <sub>13</sub> O <sub>3</sub> Re	C <sub>10</sub> H <sub>13</sub> O <sub>4</sub> Re
Formula weight	441.48	453.49	475.49	491.49
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	<i>P</i> 2(1)/n	C2(1)/c
a (Å)	8.8485(5)	10.7799(10)	8.9367(4)	32.844(3)
b (Å)	13.8341(7)	8.6629(8)	12.1360(7)	7.0582(6)
<i>c</i> (Å)	12.1274(6)	16.5270(16)	14.6388(8)	14.3171(12)
α (°)	90	90	90	90
β (°)	97.106(5)	102.575(2)	96.339(5)	101.120(2)
γ (°)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1473.13(14)	1506.4(2)	1577.96(14)	3256.7(5)
Ζ	4	4	4	8
$D_{\text{Calcd}}$ (g cm <sup>-3</sup> )	1.991	2.000	2.002	2.005
$\mu (\rm{mm}^{-1})$	8.252	8.073	7.712	7.482
F (0 0 0)	840	864	904	1872
Crystal size (mm)	$0.37 \times 0.32 \times 0.08$	$0.42 \times 0.40 \times 0.33$	$0.37 \times 0.27 \times 0.06$	$0.40 \times 0.27 \times 0.14$
heta range (°)	3.07-26.37	2.53-25.01	3.05-26.37	2.53-25.02
Reflections collected/unique	9081/3007	7253/2663	7152/3222	8086/2873
R(int)	0.0484	0.0397	0.0905	0.0943
Completeness to $\theta$	99.9%	99.9%	99.8%	99.8%
Absorption correction		Semi-empirical f	from equivalents	
Max./min. transmission	1.00000/0.37965	0.1759/0.1326	1.00000/0.04008	0.4206/0.1538
Refinement method		Full-matrix leas	st-squares on F <sup>2</sup>	
Data/restraints/parameters	3007/0/184	2663/0/190	3222/0/209	2873/0/218
Goodness of fit on F <sup>2</sup>	1.037	1.063	1.049	1.063
$R_{1}, wR_{2} [l > 2\sigma(l)]$	0.0337, 0.0799	0.0323, 0.0734	0.0648, 0.1582	0.0615, 0.1541
$R_1, wR_2$ (all data)	0.0396, 0.0843	0.0531, 0.0806	0.0753, 0.1708	0.0749, 0.1653
Max. peak (e Å <sup>-3</sup> )	1.433	2.141	3.817	4.208
Min. peak (e Ă <sup>-3</sup> )	-1.492	-0.996	-4.064	-3.236
CCDC	1424780	1424779	1424777	1424778

Table 1. Crystal data and structure refinement parameters for 9, 10, 12, and 13.

( $\lambda = 0.71073$  Å) radiation using the  $\varphi/\omega$  scan technique at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using SHELXL-97. All hydrogens were placed at their calculated positions and treated as riding. The molecular graphics in this manuscript were done using Diamond software [26]. The crystal data and summary of X-ray data collection are presented in table 1.

#### 2.10. Catalytic tests

The catalytic reactions were carried out under an argon atmosphere with magnetic stirring; the required complexes (0.02 mmol) were mixed with 1,2-dichloroethane (3.5 mL) in a 25 mL round-bottom flask at room temperature. Aromatic compounds and alkylation/acylation reagents were added by syringe. The reaction mixture was heated in an oil bath at 84 °C for 15 and 24 h. After cooling to room temperature, the solid catalyst was separated from the reaction mixture by filtration, solvent was removed through rotary evaporation, and the residue was purified by  $Al_2O_3$  column chromatography, eluting with petroleum ether to give the corresponding products. The progress of the reaction was monitored using an Agilent 6820 gas chromatograph.

#### 3. Results and discussion

#### 3.1. Preparation of the complexes

The ligand precursors  $[C_9H_7R]$   $[R = {}^nBu$  (1),  ${}^tBu$  (2), CH(CH<sub>2</sub>)<sub>4</sub> (3), Ph (4), Bz (5), C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> (6), C<sub>6</sub>H<sub>4</sub>Cl (7)] were reacted with Re<sub>2</sub>(CO)<sub>10</sub> in refluxing decalin for 24 h to give the corresponding complexes  $[(\eta^{5-}C_9H_6R)Re(CO)_3]$   $[R = {}^nBu$  (8),  ${}^tBu$  (9), CH(CH<sub>2</sub>)<sub>4</sub> (10), Ph (11), Bz (12), C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub> (13), C<sub>6</sub>H<sub>4</sub>Cl (14)] (scheme 1). These reactions were carried out in refluxing decalin, which indicates that these ligands have low reactivity towards Re<sub>2</sub>(CO)<sub>10</sub>. IR spectra of 8–14 showed similar patterns and displayed strong absorptions in the terminal *v*(CO) region. <sup>1</sup>H NMR spectra of 8–14 were similar and showed peaks at 5.45–5.95 ppm for the C5-ring protons of the indenyl ligands. <sup>1</sup>H NMR spectrum of 9 showed a singlet at 1.49 ppm for the *t*-butyl protons. <sup>1</sup>H NMR spectra of 13 showed a singlet at 3.86 ppm for the methoxy protons.

#### 3.2. Crystal structures of 9, 10, 12, and 13

The crystal structures of **9**, **10**, **12**, and **13** were determined by X-ray diffraction. Selected bond parameters for these complexes are presented in table 2 and their structures are depicted in figure 1.



Scheme 1. Synthesis of 8–14.

6		10		12		13	
Bond distances							
Re(1)–C(1)	2.329(5)	Re(1)–C(1)	2.307(8)	Re(1)–C(1)	2.306(9)	Re(1)–C(1)	2.309(10)
3e(1)–C(2)	2.289(6)	Re(1)–C(2)	2.275(7)	Re(1)–C(2)	2.291(10)	Re(1)–C(2)	2.310(11)
Re(1)–C(3)	2.281(5)	Re(1)–C(3)	2.280(8)	Re(1)–C(3)	2.276(11)	Re(1)–C(3)	2.300(13)
Re(1)–C(4)	2.352(5)	Re(1)–C(4)	2.353(7)	Re(1)–C(4)	2.371(9)	Re(1)–C(4)	2.385(10)
Re(1)–C(5)	2.375(5)	Re(1)–C(5)	2.386(7)	Re(1)–C(5)	2.368(10)	Re(1)–C(5)	2.363(10)
{e(1)–C(14)	1.919(7)	Re(1)–C(15)	1.916(9)	Re(1)–C(17)	1.915(11)	Re(1)–C(17)	1.949(12)
{e(1)–C(15)	1.926(6)	Re(1)–C(16)	1.894(8)	Re(1)–C(18)	1.907(11)	Re(1)–C(18)	1.915(14)
{e(1)–C(16)	1.903(6)	Re(1)–C(17)	1.876(8)	Re(1)–C(19)	1.917(12)	Re(1)–C(19)	1.916(13)
le(1)–CEN	1.982	Re(1)–CEN	1.975	Re(1)–CEN	1.980	Re(1)–CEN	1.984
sond angles							
:(16)-Re(1)-C(14)	89.5(3)	C(17)–Re(1)–C(16)	90.7(3)	C(18)-Re(1)-C(17)	89.1(4)	C(18)-Re(1)-C(19)	88.7(5)
C(16)-Re(1)-C(15)	90.4(2)	C(17)–Re(1)–C(15)	87.9(3)	C(18)–Re(1)–C(19)	91.3(4)	C(18)-Re(1)-C(17)	91.8(5)
C(14)-Re(1)-C(15)	89.9(3)	C(16)–Re(1)–C(15)	91.9(3)	C(17)–Re(1)–C(19)	89.6(5)	C(19)–Re(1)–C(17)	88.3(5)
C(13)-C(10)-C(12)	108.5(5)	C(12)-C(11)-C(10)	105.5(8)	C(16)-C(11)-C(10)	123.3(10)	C(15)-C(10)-C(1)	121.3(9)
C(13)-C(10)-C(11)	108.7(6)	C(11)-C(10)-C(14)	103.2(7)	C(12)-C(13)-C(14)	121.1(11)	C(14)-C(13)-O(1)	116.0(10)
C(12)-C(10)-C(11)	109.2(5)	C(13)-C(14)-C(10)	103.3(8)	C(16)-C(15)-C(14)	119.9(11)	C(13)-O(1)-C(16)	118.6(9)
<b>Dihedral angles between</b>	the 5 and 6 memb	ered indenyl fragments					
3.84		4.19		3.20		2.20	

Z. MA ET AL. 714



Figure 1. The molecular structures of 9, 10, 12, and 13. Ellipsoids correspond to 50% probability. Hydrogens are omitted for clarity.

X-ray diffraction analyses confirm that **9**, **10**, **12**, and **13** are similar mononuclear-substituted indenyl rhenium carbonyl complexes, in which rhenium is  $\eta^5$ -coordinated to the five-membered ring of the indenyl group and three terminal CO ligands. The Re–C distances to the indenyl ring carbons in these complexes show the typical pattern of longer distances to the ring fusion carbons than to the three "allylic" carbons. These differences are similar to values found for similar Re indenyl complexes, like (CMe<sub>2</sub>)(C<sub>9</sub>H<sub>7</sub>)( $\eta^5$ -C<sub>9</sub>H<sub>6</sub>)Re(CO)<sub>3</sub> [27]. Of the three Re–C distances to the "allylic" carbons, the Re(1)–C(1) distance is longer than the other two, which is attributed to the bulky substituent on C(1). The Re–CEN (CEN means centroid of the cyclopentadienyl ring) distances are 1.982 Å for **9**, 1.975 Å for **10**, 1.980 Å for **12** and 1.984 Å for **13**, respectively, which are attributed to the steric effect of the indenyl substituents. The dihedral angles between the five- and six-membered indenyl fragments are 3.84° for **9**, 4.19° for **10**, 3.20° for **12** and 2.20° for **13**.

In the crystal of **9**, there are two  $\pi$ - $\pi$  interactions with centroid–centroid distances of 3.831(4) and 3.454(3) Å (symmetry operation: 2 - x, -y, 2 - z). These distances in **10** are 3.441(5) and 3.430(4) Å (symmetry operation: -x, 2 - y, -z). The dihedral angles between them are  $\alpha = 3.9(3)^{\circ}$  in **9** and  $0.0(5)^{\circ}$  in **10**, and the corresponding slipping angles are  $\beta = 24.7$ ,  $\gamma = 25.6^{\circ}$  in **9** and  $\beta = \gamma = 4.6^{\circ}$  in **10**. The intermolecular  $\pi$ - $\pi$  stacking interactions affect the molecular distortions of these complexes in which the smallest bond angle of C–Re–C is  $35.10(17)^{\circ}$  for **9**,  $35.7(3)^{\circ}$  for **10**,  $34.4(5)^{\circ}$  for **12** and  $35.4(4)^{\circ}$  for **13**.

#### 3.3. Catalytic studies

To develop an optimal catalytic system, we investigated substituted indenyl rhenium carbonyl complex **12** as a precatalyst on the Friedel-Crafts reaction of anisole and *tert*-butyl chloride (scheme 2 and table 3). A solution of anisole (2 mmol) and *tert*-butyl chloride (6 mmol) in 1,2-dichloroethane (3.5 mL) was refluxed in the presence of a catalytic amount of the precatalyst (2 mol%) under argon. By refluxing in 1,2-dichloroethane, mixtures of *mono-* and *di*-substituted products were obtained. The conversion rate reached as high as 89.5% for *para*-selectivity with 5 h reaction time (table 3, entry 3). The effect of different solvents on catalytic efficacy was also studied, with the reaction conversion rate decreasing significantly, when cyclohexane (boiling point of 80.7 °C) was chosen as the solvent under the same conditions. The lower yield was ascribed to the lower polarity of cyclohexane. The experiment was carried out in the absence of **12** and no products were obtained, which suggested that electrophilic-substitution mechanism was involved in **12**; further studies will be needed to elucidate the mechanism of these catalytic reactions.

In order to test the capability of Friedel-Crafts alkylation reactions (scheme 2) catalyzed by these substituted indenyl rhenium carbonyl complexes, influencing factors such as reaction time, yield, and economic considerations were considered. The following experimental conditions were chosen for further work: 1,2-dichloroethane as solvent; the molar ratio 1:3 of aromatic substrates and alkylation reagents; the amount 0.02 mmol of catalyst; temperature 84 °C; reaction time 15 h. The catalytic results are shown in table 4. The catalytic activities of the reported complexes were determined from % yield and the turnover (T.O.) conversion of substrate as follows:

Yield (%) = [Wt. of alkylation substrate (product)/Wt. of theoretical yield]  $\times$  100 (1)



Scheme 2. Friedel-Crafts alkylation reactions of anisole, phenol, and toluene with alkylation reagents.

Entry	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Yield (%) (mono-/di-)
1	CICH,CH,CI	25	24	3.0 (100:0)
2	2 2	60	24	10.6 (95:5)
3		84	5	89.5 (65:35)
4		84	15	90.3 (61:39)
5	CHCI,	61	15	88.3 (22:78)
6	Cyclohexane	80	15	15.8 (91:9)

 Table 3. Optimization of 12 catalyzed Friedel-Crafts alkylation reaction.

Notes: Reagents and conditions: anisole (2 mmol); *tert*-butyl chloride (6 mmol);  $[(\eta^5-C_9H_6CH_2C_6H_5)Re(CO)_3]$  (2 mol%); solvent (3.5 mL).

derivatives Re	-					L								
OMe	eagents	catalyzed	by <b>8</b>	-	TON TOF	di-) cat	alyzed by	7-/ 12 TON	TOF	cat	(%)(()()()()()()()()()()()()()()()()()(	TON	TOF	
	<sup>t</sup> BuCl	91.4 (68:	32)		91.4 6.1	89.	7 (66:34)	89.7	6.0	6	1.4 (60:40)	91.4	6.1	
>	'BuBr	96.1 (51:	49)		96.1 6.4	97.	6 (55:45)	96.1	6.4	6	96.7 (58:42)	96.1	6.4	
	"BuBr	32.4 (100	(0:		32.4 2.2	30.	2 (100:0)	30.2	2.0	2	(0:00:0)	26.9	1.8	
HO (	'BuCl	95.9 (88:	12)		95.9 6.4	95.	5 (79:21)	95.5	6.4	6	95.7 (84:16)	95.5	6.4	
>	'BuBr	97.1 (93:	7)		97.1 6.5	98.	2 (89:11)	98.2	6.5	6	8.5 (90:10)	98.2	6.5	
	"BuBr	0			0 0	0		0	0		0	0	0	
We	'BuCl	68.4 (100	(0:		68.4 4.6	78.	4 (100:0)	78.4	5.2	7	'1.0 (100:0)	71.0	4.7	
>	fBuBr	79.3 (100	(0:		79.3 5.3	83.	5 (100:0)	83.5	5.6	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	32.2 (100:0)	82.2	5.5	
	"BuBr	0			0 0	0		0	0		0	0	0	
Benzene	Yield (%)(n	(-ip/-ouor	Ĩ	L C F	Yield (%)(mono-/di-	(-	Ϋ́	ield (%)(mono-,	/di-)	C F	Yield (%)(mon	o-/di-)	C F	
derivatives Keagen	catalyze			2 3			5		<b>5</b>		r catalyzed by	<b>1</b>		
	,) č. <del>,</del> 94.5 (,	(87:7	94.3	0.3	(45:10) 2.04	90.3	0.0	(cc:co) c.26	72.	0.7	2 93.4 (00:4	U) <del>9</del> 3.	4 0.7	
<sup>t</sup> BuBr	97.7 (5	5:45)	97.7	6.5	98.1 (56:44)	98.1	6.5	97.3 (59:41)	97.	3.6.5	5 96.9 (55:4	5) 96.	9 6.5	
"BuBr	40.2 (1	0:00	40.2	2.7	28.4 (100:0)	28.4	1.9	26.7 (100:0)	26.	7 1.8	3 29.8 (100:	0) 29.	8 2.0	
OH (BuCl	95.8 ({	37:13)	95.8	6.4	97.9 (85:15)	97.9	6.5	96.0 (80:20)	96.	0 6.4	4 94.2 (86:1	4) 94.	2 6.3	
'BuBr	3) 8.86	36:14)	98.8	6.6	99.1 (90:10)	99.1	6.6	99.2 (91:9)	.66	2 6.6	5 98.9 (92:8	) 98.	9 6.6	
"BuBr	0		0	0	0	0	0	0	0	0	0	0	0	
Me 'BuCl	76.2 (1	(0:00)	76.2	5.1	73.4 (100:0)	73.4	4.9	70.8 (100:0)	70.	8	7 80.4 (100:	0) 80.	4 5.4	
'BuBr	83.2 (1	(0:00)	83.2	5.5	80.2 (100:0)	80.2	53	81.3 (100:0)	81.	2 <sup>.</sup> .	4 83.5 (100:	0) 83.	5 5.6	
Iana	>		5	5	D	5	5	5	Þ	>	Þ	S	>	

**Table 4**. Catalvzed Eriedel-Crafts alkvlation reaction of aromatic substrates with different alkvlation reagents.

JOURNAL OF COORDINATION CHEMISTRY 😔 717

718 👄 Z. MA ET AL.

TON = turnover number [(mol of product)/(mol of catalyst)](2)

$$TOF = TON/reaction time (15 h)$$
 (3)

All seven complexes were capable of catalyzing Friedel-Crafts alkylation reactions; the yields and turnovers vary with the different catalysts used, as indicated in table 4. In no case was there any detectable alkylation product in the absence of the rhenium complexes. The relatively higher product yield obtained for alkylation of anisole and phenol than for toluene was due to the fact that aromatic substrates containing electron-donating groups tend to improve the yield of these Friedel-Crafts reactions. The smaller influence of the different substituents on the catalytic behavior may be due to their modest variations in steric and electronic properties. The aryl products were obtained in moderate-to-good yields with high *para*-selectivities. The pattern of results suggests that the reactions proceed by an electrophilic-substitution mechanism [28, 29]. *Tert*-butyl halides could be used as alkylation reagents in these reactions and the corresponding aryl products were obtained in good yields with high selectivity for the *para*-products. The reactivity of *tert*-butyl bromide was higher than that of *tert*-butyl chloride, since bromide is a better leaving group. The order of increasing reactivity was *n*-butyl bromide < *tert*-butyl chloride < *tert*-butyl bromide, which was consistent with the classical Friedel-Crafts mechanism.

With the promising results of catalytic Friedel-Crafts alkylation reactions, the study was then extended to the Friedel-Crafts acylation (scheme 3) using these complexes as catalysts. Three acylation reagents were employed, including benzoyl chloride, phenylacetyl chloride, and cinnamoyl chloride. The acylation reactions were carried out under the following conditions: 1,2-dichloroethane as solvent; the molar ratio 1:3 of aromatic substrates and acylation reagents; the amount 0.02 mmol of catalyst; temperature 84 °C; reaction time 24 h. The catalytic results are shown in table 5.

With the above studies, all seven complexes catalyze Friedel-Crafts acylation reactions. The yields and turnovers vary with the different catalysts used as indicated in table 5. Compared with the alkylation reaction, TONs and TOFs of acylation are much lower than alkylation, thus the yields of alkylation are much higher than acylation. Friedel-Crafts reactions are electrophilic substitution reactions, however, the halogen and the carbonyl caused p-pi conjugation in the acylating agent, thus loss of the halogen to form the carbocation was difficult. Benzoyl chloride and phenylacetyl chloride were used as acylation reagents in these reactions and the corresponding acyl products were obtained with high selectivity for the *para*-products without detection of di-substituted products, suggesting that the



R<sup>1</sup>=OMe, R<sup>2</sup> = Ph (**18**); PhCH<sub>2</sub> (**19**); PhCH=CH (**20**); R<sup>1</sup>=Me, R<sup>2</sup> = Ph (**21**); PhCH<sub>2</sub> (**22**)



Table 5.	Catalyzed Frie	del-Crafts	acylation re	action of a	aromat	ic subs	trates with dil	ferent acy	rlation r	eagents.						
Entry	Benzene deri	vatives	Reagents	Yield (%)	catalyzı	ed by <b>8</b>	TON	TOF Yi	eld (%) c	catalyzed by <b>9</b>	TON	TOF	Yield (%) catalyzed l	by <b>10</b> T	L NO	ОF
-	-OMe		Phcc1		38.9		38.9	2.6		45.3	45.3	3.0	40.8	4	8.04	2.7
2	>		0    PhCH <sub>2</sub> CCI		36.2		36.2	2.4		38.6	38.6	2.6	38.0	(m)	88.0	2.5
£		P	hcH == cHccl		20.6		20.6	1.4		26.3	26.3	1.8	22.6		22.6	1.5
4	M-C		Phccl Phccl		30.1		30.1	2.0		36.1	36.1	2.4	30.7	m	30.7	2.0
5	>		0    PhCH <sub>2</sub> CCI		22.7		22.7	1.5		24.8	24.8	1.7	25.8	7	25.8	1.7
Entry	Benzene	Descente	Yield (%) cã	atalyzed	NOT	Ϋ́Ι	ield (%) catalyz	ed TON	TOF	Yield <sup>b</sup> (%) catal ایر <b>13</b>	yzed	NO	Yield (%) cataly: کت این ۲۸	zed		ц
	derivatives	кеадепть	- Ya	_		5	ay Iz	NON NON	2	0 IS			JF DY 14	_		5
-	oMe	0 PhCCI	50.2	6	50.2	3.3	42.3	42.3	2.8	56.2	-,	56.2 3	.7 41.9	4	1.9	2.8
2		0 II PhCH <sub>2</sub> CCI	46.4	+	46.4	3.1	41.6	41.6	2.8	42.5	7	ł2.5 2	.8 40.3	4	0.3	2.7
£		0 II PhCH == CHCCI	21.6	10	21.6	1.4	23.6	23.6	1.6	19.6	,	1 9.6	.3 30.4	30	0.4	2.0
4	¶-√	PhCCI	28.9	0	28.9	1.9	32.1	32.1	2.1	40.5	7	40.5 2	.7 31.6	'n	1.6	2.1
5	,	0 II PhCH <sub>2</sub> CCI	23.5	10	23.5	1.6	20.8	20.8	1.4	23.9		23.9 1	.6 24.5	5	4.5	1.6
Notes: Re	agents and cond	itions: benze	ene derivatives	s (2 mmol); r	eagents	(6 mmo	l); catalyst (0.02	mmol); solv	ent 3.5 m	ıL, 84 °C; 24 h. The	yield was	based o	n benzene derivative	ŝ		

ä i+h 4 ų Č 4 Ľ Ľ

720 😔 Z. MA ET AL.

catalytic reaction has high regioselectivity. Toluene exhibited less reactivity in the Friedel-Crafts acylation reactions than anisole. The results showed that the reaction was favored by the presence of electron-donating groups in the aromatic substrate, consistent with the characteristics of the aromatic electrophilic substitution reaction [30].

# 4. Conclusion

Reactions of substituted indenyl ligands  $[C_9H_7R]$   $[R = ^nBu (1), ^tBu (2), CH(CH_2)_4 (3), Ph (4), Bz (5), C_6H_4OCH_3 (6), C_6H_4Cl (7)]$  with Re<sub>2</sub>(CO)<sub>10</sub> in refluxing decalin were studied. A series of new mononuclear indenyl rhenium carbonyl complexes were obtained and showed their obvious catalytic activity in Friedel-Crafts reactions of aromatic substrates with alkylation and acylation reagents catalyzed by these complexes. *Tert*-butyl halides could be used as alkylation reagents in these reactions. It is consistent with an aromatic electrophilic substitution reaction that aromatic substrates containing electron-donating groups were beneficial for improving the reactivity. Compared with traditional catalysts, the present system has a significant practical advantage: lower amounts of catalysts, mild reaction conditions, high selectivity, and ease of use. To elucidate the reaction mechanism and expand the synthetic utility of these catalysts, further studies are in progress.

#### **Supplementary material**

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 1424780, 1424779, 1424777 and 1424778 for **9**, **10**, **12**, and **13**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44 1223 336 033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

# **Supplementary information**

The structure and characterization data for related catalytic products.

# **Disclosure statement**

No potential conflict of interest was reported by the authors.

# Funding

This work was supported by the National Natural Science Foundation of China [grant number 21372061]; the Hebei Natural Science Foundation of China [grant number B2013205025], [grant number B2014205018], [grant number B2015205116]; and the Key Research Fund of Hebei Normal University [grant number L2012Z02].

# References

- [1] V. Cadierno, J. Díez, M.P. Gamasa, J. Gimeno, E. Lastra. Coord. Chem. Rev., 193-195, 147 (1999).
- [2] M.J. Calhorda, V. Félix, L.F. Veiros. Coord. Chem. Rev., 230, 49 (2002).
- [3] D. Zargarian. Coord. Chem. Rev., 233-234, 157 (2002).
- [4] R.L. Halterman. Chem. Rev., 92, 965 (1992).

- [5] P.C. Möhring, N.J. Coville. J. Organomet. Chem., 479, 1 (1994).
- [6] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth. Angew. Chem., Int. Ed. Engl., 34, 1143 (1995).
- [7] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi. Chem. Rev., 100, 1253 (2000).
- [8] T.M. Frankcom, J.C. Green, A. Nagy, A.K. Kakkar, T.B. Marder. Organometallics, 12, 3688 (1993).
- [9] C. Bonifaci, A. Ceccon, S. Santi, C. Mealli, R.W. Zoellner. Inorg. Chim. Acta, 240, 541 (1995).
- [10] M.P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, B.M. Martín-Vaca, D. Monti, M. Bassetti. Organometallics, 15, 302 (1996).
- [11] Z.H. Ma, F. Li, X.H. Liu. J. Lin. Chin. J. Org. Chem., 29, 1294 (2009).
- [12] K.M. Guo, Z.H. Ma, S.Z. Li, Z.G. Han, J. Lin, X.Z. Zheng. Chin. J. Inorg. Chem., 28, 643 (2012).
- [13] Z.H. Ma, D. Fan, S.Z. Li, Z.G. Han, X.Y. Li, X.Z. Zheng, J. Lin. New J. Chem., 39, 1075 (2015).
- [14] G.W. Coates, R.M. Waymouth. Science, 267, 217 (1995).
- [15] M.D. Bruce, G.W. Coates, E. Hauptman, R.M. Waymouth, J.W. Ziller. J. Am. Chem. Soc., 119, 11174 (1997).
- [16] R. Kravchenko, A. Masood, R.M. Waymouth, C.L. Myers. J. Am. Chem. Soc., 120, 2039 (1998).
- [17] F. Zhang, Y. Mu, L. Zhao, Y. Zhang, W. Bu, C. Chen, H. Zhai, H. Hong. J. Organomet. Chem., 613, 68 (2000).
- [18] F. Zhang, Y. Mu, J. Wang, Z. Shi, W. Bu, S. Hu, Y. Zhang, S. Feng. Polyhedron, 19, 1941 (2000).
- [19] S. Kirchberg, D.R. Fröhlich, P.D.A. Studer. Angew. Chem. Int. Ed., 49, 6877 (2010).
- [20] S. Rahmani, A.A. Entezami. J. Mol. Catal. A: Chem., 320, 27 (2010).
- [21] M.H. Qi, Q. Shen, X.Q. Gong, Z.Q. Shen, L.H. Weng. Chin. J. Chem., 20, 564 (2002).
- [22] K. Hermann, D.A. Turner, C.M. Hadad, J.D. Badjić. Chem. Eur. J., 18, 8301 (2012).
- [23] K.E. du Plooy, J. du Toit, D.C. Levendis, N.J. Coville. J. Organomet. Chem., 508, 231 (1996).
- [24] N.S. Mills, K.B. Llagostera, C. Tirla, S.M. Gordon, D. Carpenetti. J. Org. Chem., 71, 7940 (2006).
- [25] S.K. Kim, H.K. Kim, M.H. Lee, S.W. Yoon, Y. Do. Chem. Eur. J., 13, 9107 (2007).
- [26] K. Brandenburg. Diamond Version 3.2K, Crystal Impact GbR, Bonn, Germany (1997–2014).
- [27] B.L. Zhu, W. Shi, Y.F. Chen, Y. Li, X.T. Hao. Inorg. Chim. Acta, 405, 485 (2013).
- [28] S. Sebti, R. Tahir, R. Nazih, S. Boulaajaj. Appl. Catal. A: Gen., 218, 25 (2001).
- [29] Y. Nishiyama, F. Kakushou, N. Sonoda. Bull. Chem. Soc. Jpn., 73, 2779 (2000).
- [30] H. Kusama, K. Narasaka. Bull. Chem. Soc. Jpn., 68, 2379 (1995).