PAPER

Synthesis, structures and catalytic activity of cyclometalated rhenium complexes†

Ruichen Sun, Tian Wang, Shaowei Zhang, Xiaodan Chu and Bolin Zhu*

Thermal reactions of aryl-substituted phosphines or phosphinites with $Re_2(CO)_{10}$ in chlorobenzene resulted in the corresponding five-membered cyclometalated rhenium complexes (**1–5**) *via* an intramolecular activation of the $C(sp^2)$–H or $C(sp^3)$–H bond. The only exception occurred in the case of (1-naphthyl) diisopropylphosphinite, which gave a diphosphinite-substituted dinuclear rhenium complex **6**. Competition reaction indicated that the aromatic $C(sp^2)$–H bond is more likely to be activated than the $C(sp^3)$–H bond under the same conditions. Photolysis of **1** or **2** in CHX_3 led to the cleavage of the Re–C σ bond to yield corresponding phosphine-substituted tetracarbonyl rhenium halides **7–10**. Complex **1** reacted with CF_3COOH in CH_2Cl_2 to give addition product **11**. Photolysis of cyclorhenated complexes **1–3** with a series of aryl halides in benzene resulted in the stoichiometric formation of biphenyl, together with corresponding phosphine-substituted tetracarbonyl rhenium halides (**7**, **9**, **10**, **12**, and **13**). When base was introduced into the above reaction, a catalytic system was established. Under optimized conditions, complex **1** provided moderate yield of biphenyl in a couple of hours at a [Re] : substrate ratio of 1 : 200. Molecular structures of complexes **1**, **6**, **9**, and **11** were determined by X-ray diffraction.

Introduction

Cyclometalation has always been one of the most widely investigated reactions in the field of organometallic chemistry since it was first discovered in the early 1960s.[1] The reason that cyclometalation has received such considerable attention is mainly due to the following three aspects: (i) it represents probably the mildest route for the intramolecular activation of C–H bonds, and forms a cyclometalated complex containing a new M–C σ bond. (ii) Cyclometalated complexes have wide applications in many fields, such as photosensitizers for solar cells[2] and OLED materials.[3] (iii) As catalysts for a wide range of reactions, including metathesis reactions,[4] cross-coupling reactions,[5] and transfer hydrogenation reactions.[6] Of all transition metals, cyclometalated rhenium complexes have recently attracted more and more attention due to their luminescent properties, which may have potential as liquid crystals,[7] and in particular, their indispensable role in many catalytic cycles, including the rhenium-catalyzed annulation reaction of aromatic imines with alkynes,[8] alkenes,[9] or aldehyde,[10] and alkylation of 2-phenyl, or alkenyl-substituted pyridine.[11] Generally, the most widely used precursors for cyclorhenation are $Re(X)(CO)_5$ (X = H, Me, Cl, or Br) and $Re(Cp)L_3$ (L = CO, PR$_3$,

Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic–Organic Hybrid Functional Material Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, PR China. E-mail: hxxyzbl@gmail.com; Fax: +86-22-23766532; Tel: +86-22-23766515

† CCDC 1520723–1520726. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ra28263f

or a mixture thereof). In this paper, we report the synthesis of a series of cyclometalated rhenium complexes starting from the precursor $Re_2(CO)_{10}$, as well as their catalytic activity in direct arylation of arenes with aryl halides.

Results and discussion

Reaction of $Re_2(CO)_{10}$ with (1-naphthyl)diphenyl phosphine or diisopropyl(1-naphthyl) phosphine

A solution of $Re_2(CO)_{10}$ and 2 equiv. of (1-naphthyl) phosphine or diisopropyl(1-naphthyl) phosphine in chlorobenzene was refluxed overnight to result in corresponding five-membered cyclorhenated complex **1** or **2** in good yields (Scheme 1). Obviously, the formation of complexes **1** and **2** goes through an intramolecular activation of $C(sp^2)$–H bond on the adjacent α position of naphthyl ring. The ^{1}H NMR spectrum of **1** showed six peaks centered at δ 8.21 (1H), 7.95 (1H), 7.68 (1H), 7.60 (1H), 7.55–7.49 (1H, overlapping with peaks for protons on two phenyl rings), 7.35 (1H) corresponding to six protons of the metalated naphthyl group. More distinctly, the ^{1}H NMR
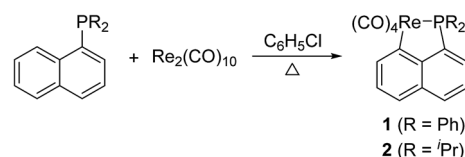
Scheme 1 Reactions of 1-naphthyl-substituted phosphines with $Re_2(CO)_{10}$.

spectrum of **2** exhibited five well-separated multiplets at δ 8.16 (1H), 7.85 (1H), 7.58 (2H), 7.43 (1H), 7.28 (1H) for resonance of six protons on the metalated naphthyl group. The IR spectra of **1** and **2** (KBr film) indicated the expected strong $\nu(CO)$ absorptions in the range 2084–1925 cm^{-1} for terminal carbonyls. The structure of **1** was further confirmed by single-crystal diffraction analysis, which is shown in Fig. 1, with selected bond lengths and angles. It reveals an octahedral geometry with the rhenium(I) center coordinated by four carbonyl groups, one phosphorus atom P(1), and one metalated carbon atom C(3), in which P(1) and C(3) are mutually adjacent. Re–P bond length is 2.4413(9) Å, a litter longer than that (2.428(3) Å) in four-membered cyclorhenated analogue Re(CO)$_4$(PPh$_2$CH$_2$CH$_2$).[12]

Reaction of Re$_2$(CO)$_{10}$ with diisopropyl(*o*-methylphenyl) phosphine

Having demonstrated that phosphine ligand could be employed as a donor group for metalation of a naphthyl C(sp^2)–H bond in complexes **1** and **2**, we decided to test whether it could also promote activation of a C(sp^3)–H bond. The corresponding reaction of Re$_2$(CO)$_{10}$ with diisopropyl(*o*-methylphenyl) phosphine was carried out, which afforded a product **3** in 50% yield (Scheme 2). The ^{1}H NMR spectrum of **3** showed three multiplets at δ 7.38 (1H), 7.24 (2H), 7.04 (1H) duo to four protons on the phenyl ring, one multiplet at δ 2.49 (2H) for methenyl signal, and two doublets of doublets at δ 1.20 (6H) and 1.05 (6H) for signals of four methyls on two isopropyl groups. However, there was no signal for the methyl on the phenyl ring; instead one multiple at δ 2.50, integrating to 2H, assigned to a metal-bound
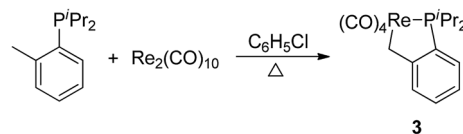
Scheme 2 Reaction of diisopropyl(*o*-methylphenyl) phosphine with Re$_2$(CO)$_{10}$.

CH$_2$. These resonances confirm the expected C(sp^3)–H bond activation.

Reactions of Re$_2$(CO)$_{10}$ with diisopropyl(2-methylnaphthyl) phosphine

Since both C(sp^2)–H bond and C(sp^3)–H bond could be activated in cyclometalation of Re$_2$(CO)$_{10}$ with phosphines, we were curious about the relative activity between them. Therefore, diisopropyl(2-methylnaphthyl) phosphine was chosen as the ligand, which provides both C(sp^2)–H and C(sp^3)–H bonds at the appropriate positions, to test the competition reaction. Therefore, reaction of Re$_2$(CO)$_{10}$ with diisopropyl(2-methylnaphthyl) phosphine under the above-mentioned conditions was performed, which gave a product **4** (Scheme 3). The ^{1}H NMR spectrum of **4** showed four multiplets in the aromatic region, all integrating to 5H due to the naphthyl ring, and a doublet at δ 2.71, assigned to signal for the methyl on the naphthyl ring. These resonances indicated that the aromatic C(sp^2)–H bond is selectively activated in the reaction to form the five-membered cyclometalated complex **4**. The reason that the aromatic C(sp^2)–H bond activation is favored over C(sp^3)–H bond activation is probably owing to the higher thermal stability of aryl hydrogen activated product when compared to alkyl hydrogen activated product.

Reactions of Re$_2$(CO)$_{10}$ with phosphinites

In order to explore applicable scope of this type of cyclometalation, ligand was extended to phosphinite. Therefore reaction of Re$_2$(CO)$_{10}$ with *o*-methylphenyl diisopropylphosphinite was examined, which produced the corresponding five-membered cyclometalated complex **5** (Scheme 4). The ^{1}H NMR spectrum of **5** showed three multiplets (δ 7.55, 6.84, and 6.71) in the aromatic region, each integrating to 1H due to the phenyl ring, and a singlet at δ 2.25, assigned to signal for the methyl on the phenyl ring. These ^{1}H NMR information confirms an *ortho* aromatic C(sp^2)–H bond activation.

However, when Re$_2$(CO)$_{10}$ reacted with another phosphinite, 1-naphthyl diisopropylphosphinite under the above-mentioned conditions, the reaction did not produce the similar five-
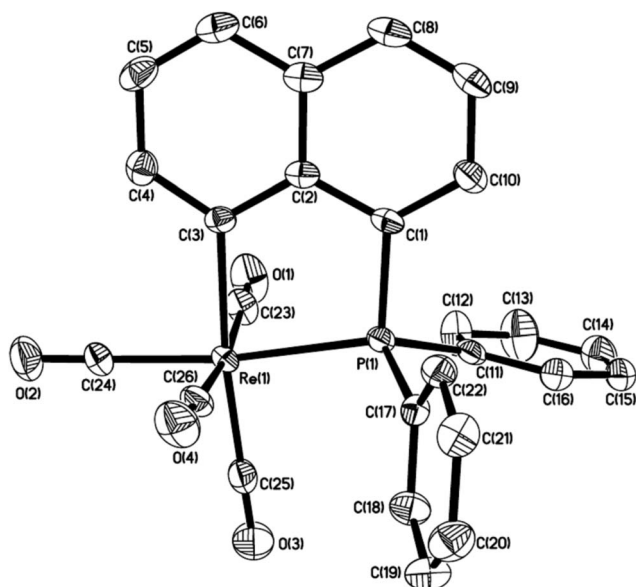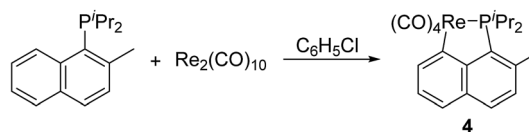

Fig. 1 Thermal ellipsoid drawing of **1** showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Re(1)–P(1) 2.4413(9), P(1)–C(1) 1.812(3), Re(1)–C(23) 1.987(4), Re(1)–C(24) 1.960(4), Re(1)–C(25) 1.969(4), Re(1)–C(26) 2.003(4), ∠C(3)–Re(1)–C(25) 173.87(14), ∠C(24)–Re(1)–P(1) 170.15(12), ∠C(23)–Re(1)–C(26) 171.80(16), ∠C(3)–Re(1)–P(1) 79.05(9), ∠Re(1)–P(1)–C(1) 103.52(12).

Scheme 3 Reaction of diisopropyl(2-methylnaphthyl) phosphine with Re$_2$(CO)$_{10}$.
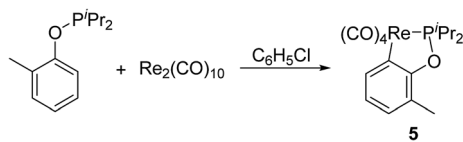
Scheme 4 Reaction of o-methylphenyl diisopropylphosphinite with $Re_2(CO)_{10}$.

Scheme 5 Reaction of 1-naphthyl diisopropylphosphinite with $Re_2(CO)_{10}$.

Scheme 6 Photolysis of **1** or **2** in CHX_3 (X = Cl, Br).

7 (R = Ph, X = Cl)
8 (R = ^{i}Pr, X = Cl)
9 (R = Ph, X = Br)
10 (R = ^{i}Pr, X = Br)

membered cyclometalated complex, instead a dinuclear complex **6** was obtained (Scheme 5). The ^{1}H NMR spectrum of **6** showed six multiplets in the aromatic region, all integrating to 7H corresponding to protons of the naphthyl ring. These resonances indicate the absence of aromatic $C(sp^2)$–H bond activation. The structure of **6** was further confirmed by single-crystal diffraction analysis, which is shown in Fig. 2, with selected bond lengths and angles. It consists of a pair of square pyramidal $Re(CO)_4(P)$ units linked by a Re–Re bond. Each phosphinite ligand is located at the top of the pyramid. Two sets of carbonyl groups bounded to two rhenium atoms occur as the staggered conformation. Re–Re bond length is 3.0606(5) Å, a litter longer than that (3.04 Å) in $Re_2(CO)_{10}$.[13]

Cleavage of the cyclometalated Re–C bond of 1 or 2

Lu has reported the chemical behavior of the similar N-contained cyclorhenated complexes, including the electrophilic addition reactions of cyclorhenated complexes with HBr, RCO_2H, or I_2, which caused the opening of the metallacyclic ring to generate the corresponding rhenium products.[14] For comparison of

reactivity, we similarly treated the P-contained cyclorhenated complex **1** with excess I_2 in CH_2Cl_2 at room temperature for 24 h, however, no reaction occurred. This result may indicate the higher stability of **1** when compared with N-contained analogues. Therefore we decided to try the decyclometalation of **1** or **2** under UV light conditions. A solution of complex **1** or **2** in $CHCl_3$ or $CHBr_3$ was irradiated by UV lamp to give corresponding phosphine-substituted tetracarbonyl rhenium halide **7–10** (Scheme 6). Obviously, the Re–C bond of the five-membered ring in **1** or **2** is cleavaged readily during the photolysis. Complexes **7–10** were fully characterized by spectroscopic analysis, as well as crystallographic analysis for **9**. The molecular structure of **9** was shown in Fig. 3, with selected bond lengths and angles. Pseudooctahedral geometry is observed around the Re atom. The bromine and the (1-naphthyl)diphenyl phosphine groups are cis to each other. The Re(1)–P(1) bond length is 2.5016(12) Å, longer than that (2.4413(9) Å) in five-membered cyclorhenated structure of **1**, which could be attributed to nonbonding interactions between the phosphine and $Re(CO)_4Br$ units.

Besides, for further comparison of reactivity, we also performed the photolysis of **1** with CF_3COOH. After a solution of **1**
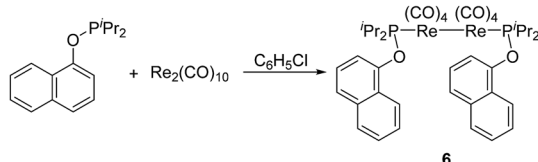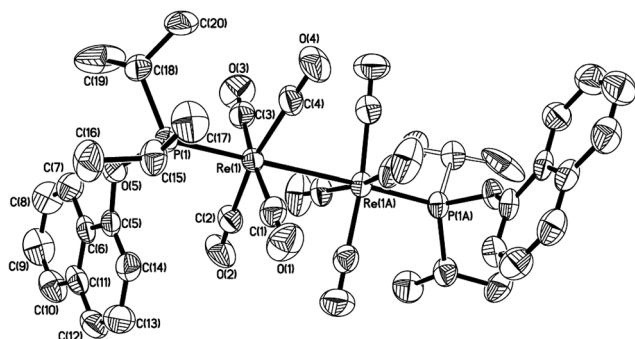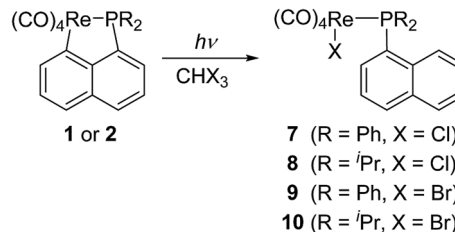

Fig. 2 Thermal ellipsoid drawing of **6** showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Re(1)–Re(1A) 3.0606(5), Re(1)–P(1) 2.3419(15), Re(1)–C(1) 1.982(10), Re(1)–C(2) 1.977(7), Re(1)–C(3) 1.977(10), Re(1)–C(4) 1.958(8), ∠P(1)–Re(1)–Re(1A) 177.56(4), ∠C(1)–Re(1)–C(3) 173.0(3), ∠C(2)–Re(1)–C(4) 168.1(3).

Fig. 3 Thermal ellipsoid drawing of **9** showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Re(1)–P(1) 2.5016(12), Re(1)–Br(1) 2.620(2), Re(1)–C(23) 2.016(6), Re(1)–C(24) 1.968(5), Re(1)–C(25) 1.997(6), Re(1)–C(27) 1.952(8), ∠P(1)–Re(1)–C(24) 176.40(16), ∠C(23)–Re(1)–C(25) 178.0(2), ∠Br(1)–Re(1)–C(27) 169.1(6).
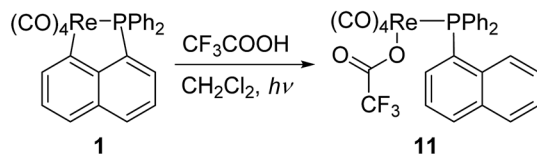
Scheme 7 Photolysis of **1** with CF_3COOH in CH_2Cl_2.

with CF_3COOH in CH_2Cl_2 was irradiated for 8 h, a white product **11** was obtained in moderate yield (Scheme 7). Complexes **11** was fully characterized by spectroscopic and crystallographic analysis. The molecular structure of **11** was shown in Fig. 4. Similarly to **9**, the pseudooctahedral geometry is observed around the Re atom. The carboxylate (CF_3CO_2) and the (1-naphthyl)diphenyl phosphine groups are *cis* to each other. The Re(1)–P(1) bond length is 2.494(2) Å, close to (2.5016(12) Å) that in **9**, but also longer than that (2.4413(9) Å) in five-membered ring structure of **1**. The formation of **11** indicates that the reactivity of **1** is similar to that of N-contained analogues when reacted with CF_3CO_2H.[14]

Photochemical reactions of 1–3 with aryl halides in benzene

We have reported the photochemical reactions of cyclopentadienylrheniumtricarbonyls [$(\eta^5-C_5R_5)Re(CO)_3$] (R = Me or H), or doubly-bridged biscyclopentadienyl dirhenium carbonyls with aryl halides in benzene, which generate biphenyl almost stoichiometrically, as well as the corresponding rhenium dicarbonyl products.[15] In order to expand the reaction scope of this type, we used cyclometalated rhenium complexes **1–3** as starting materials and tried the similar photochemical reactions with aryl halides in benzene.
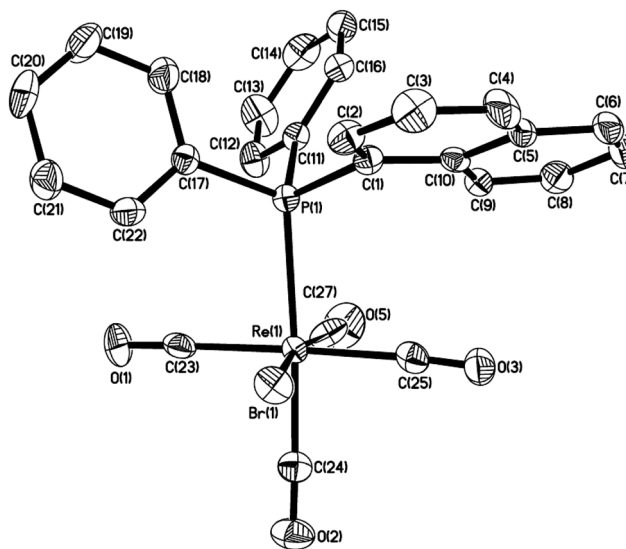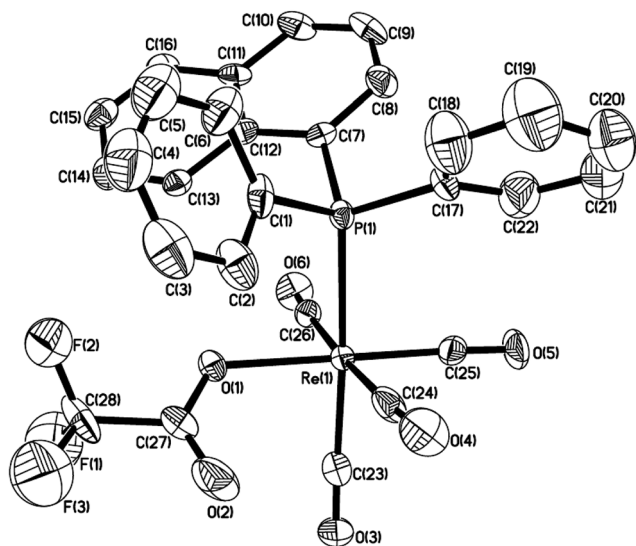

Fig. 4 Thermal ellipsoid drawing of **11** showing the labeling scheme and 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°] are Re(1)–P(1) 2.494(2), Re(1)–O(1) 2.145(5), Re(1)–C(23) 1.971(9), Re(1)–C(24) 2.007(8), Re(1)–C(25) 1.915(8), Re(1)–C(26) 2.003(8), ∠P(1)–Re(1)–C(23) 174.4(2), ∠C(24)–Re(1)–C(26) 176.4(3), ∠O(1)–Re(1)–C(25) 176.0(3).

Photolysis of **1–3** with 5 equiv. of bromobenzene in benzene under N_2 for 1–4.5 h produced a yellow solution. After removal of the solvent under vacuum, the residue was carefully separated in air by column chromatography on silica gel, and afforded the corresponding phosphine-substituted tetracarbonyl rhenium bromides **9**, **10**, and **12** (Scheme 8). Besides, the reactions also stoichiometrically produced biphenyl (92–98%, entries 1–3 in Table 1). Further activation of C–I bond and the relatively inert C–Cl bond by **1** was also conducted by photolysis of **1** with iodobenzene and chlorobenzene in benzene, which similarly provided the corresponding phosphine-substituted tetracarbonyl rhenium iodide (**13**) and chloride (**7**), as well as the biphenyl (Scheme 8) (entries 4–5, Table 1). To expand the scope of the substrates, photolysis of several *para*-substituted aryl halides with **1** were examined, and the reactions gave similarly the rhenium halides **7** or **9**, and the *para*-substituted biphenyl, no matter when the substituent is an electron-donating (MeO) or electron-withdrawing (CF_3, CH_3CO) group (entries 6–10, Table 1). Next, the source of the biphenyl was investigated. Photolysis of **1** with *p*-bromoanisole in benzene-*d*6 generated the 4-methoxybiphenyl-*d*5 (*p*-CH_3O–C_6H_4–C_6D_5), completely no biphenyl or 4,4′-dimethoxybiphenyl were observed. It is revealed that the *p*-CH_3O–C_6H_4 and C_6D_5 moieties in the resulting substituted biphenyl come from *p*-bromoanisole and solvent benzene-*d*6, respectively.

Rhenium-catalyzed direct arylation of arenes with aryl halides

On the basis of the photochemical reactions described above, we considered if the products, the phosphine-substituted tetracarbonyl rhenium halides, could revert to the original cyclometalated rhenium complexes **1–3**, then a catalytic cycle would be created. Generally, cyclometalation of the ligand-substituted rhenium halides could be realized in the presence of base. Lu has reported a cyclometalation reaction of $ReBr(CO)_4[$C(NHR)(NHPh)]$ (R = ^{i}Pr, or Pr) with Et_2NH in CH_2Cl_2 to give $Re(CO)_4[\eta^2-C(NHR)(NHPh)]$.[14] For optimization of reaction conditions, the cross-coupling of 4-bromoanisole with benzene was selected as the model reaction. The reactions were carried out with 0.5 mol% of cyclometalated rhenium complex **1** in benzene and different bases were used. Only NaOH as the base afforded the biphenyl product in moderate yield (59%, entry 1 of Table 2), whereas other tested bases such as K_2CO_3, KOAc, ^{t}BuOK, and pyrrolidine gave rise to lower yields (26–50%, entries 2–5). Other two cyclometalated rhenium complexes **2** and **3** as catalysts were also screened under the optimized conditions, complex **2** afforded slightly higher yield (68%, entry 6) than **1**, while complex **3** gave much lower yield (26%, entry 7). To expand the scope of the substrates, other aryl bromides,
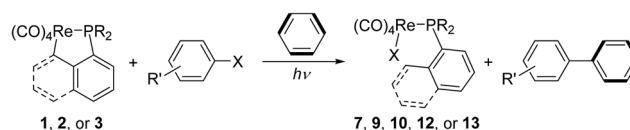
Scheme 8 Photochemical reactions of **1–3** with aryl halides in benzene.

Table 1 Photochemical reactions of **1–3** with aryl halides in benzene[a]

Entry	Re	R'	X	t [h]	Product[b]	Yield[c] [%]	Re prod.
1	**1**	H	Br	1	Biphenyl	>98	**9**
2	**2**	H	Br	1	Biphenyl	95	**10**
3	**3**	H	Br	1	Biphenyl	92	**12**
4	**1**	H	Cl	4	Biphenyl	85	**7**
5	**1**	H	I	1	Biphenyl	92	**13**
6	**1**	p-MeO	Br	4	p-MeO–biphenyl	98	**9**
7	**1**	p-CF$_3$	Br	1	p-CF$_3$–biphenyl	97	**9**
8	**1**	p-CH$_3$CO	Br	1	p-CH$_3$CO–biphenyl	80	**9**
9	**1**	p-MeO	Cl	4.5	p-MeO–biphenyl	90	**7**
10	**1**	p-CF$_3$	Cl	1.5	p-CF$_3$–biphenyl	87	**7**

[a] Reaction conditions: irradiation of **1–3** (0.10 mmol) and Ar–X (0.50 mmol) in 10 mL benzene solvent with a 500 W high-pressure Hg lamp (λ_{max} = 365 nm) in the ice-water bath. [b] Biphenyl products were isolated by routine silica gel column chromatography, and identified by comparing their respective ^{1}H NMR spectra with authentic samples. [c] Isolated yield (based on unrecovered **1–3**).

Table 2 Rhenium-catalyzed direct arylation of arenes with aryl halides[a]

Entry	Cat	Base	R'	X	t [h]	Product[b]	Yield[b,c] [%]
1	**1**	NaOH	p-MeO	Br	4	p-MeO–biphenyl	59
2	**1**	K$_2$CO$_3$	p-MeO	Br	4	p-MeO–biphenyl	30
3	**1**	KOAc	p-MeO	Br	4	p-MeO–biphenyl	26
4	**1**	^{t}BuOK	p-MeO	Br	4	p-MeO–biphenyl	50
5	**1**	Pyrrolidine	p-MeO	Br	6	p-MeO–biphenyl	29
6	**2**	NaOH	p-MeO	Br	5	p-MeO–biphenyl	68
7	**3**	NaOH	p-MeO	Br	5	p-MeO–biphenyl	26
8	**1**	NaOH	H	Br	4	Biphenyl	65
9	**1**	NaOH	p-CF$_3$	Br	3	p-CF$_3$–biphenyl	60
10	**1**	NaOH	H	Cl	8	Biphenyl	26
11	**1**	NaOH	H	I	8	Biphenyl	35

[a] Reaction conditions: irradiation of **1–3** (0.01 mmol), Ar–X (2.0 mmol), and base (2.0 mmol) in 20 mL benzene solvent with a 500 W high-pressure Hg lamp (λ_{max} = 365 nm) in the ice-water bath. [b] Biphenyl products were isolated by routine silica gel column chromatography, and identified by comparing their respective ^{1}H NMR spectra with authentic samples. [c] Isolated yield (based on unrecovered **1–3**).

including bromobenzene, and 4-bromobenzotrifluoride were examined, and the reactions afforded the corresponding biphenyl in yields of 65% and 60% (entries 8 and 9). Besides, the substrates chlorobenzene and iodobenzene were also tested using the catalyst **1**, which resulted in lower yields (26% and 35%, entries 10 and 11).

Unfortunately, rhenium catalysts **1–3** did not show higher activity to direct arylation of arenes with aryl halide under our current conditions. When we performed the photolysis of phosphine-substituted tetracarbonyl rhenium bromide **9** in benzene in the presence of NaOH, the expected cyclo-metalated rhenium complex **1** was observed, at the same time, we also obtained some free ligand, (1-naphthyl) diphenyl phosphine. Obviously, complex **9** was decomposed

partially under UV irradiation, which may explain the moderate catalytic performance of **1**. Based on the results described above, a plausible catalytic mechanism is tentatively proposed: first, a CO is dissociated from cyclometalated rhodium complexes **1–3** under UV irradiation to give a 16e$^-$ unsaturated species; this is followed by oxidative addition of a C–X bond on aryl halides (Ph–X) to form the Re(III) intermediate. In the next step, a radical aromatic substitution that involves the aromatic radical with the solvent benzene might occur to give biphenyl and the corresponding cyclometalated rhenium hydride halide complexes, which undergo reductive elimination and recoordination of CO to afford the ring-opening complexes (**7**, **9**, **10**, **12**, and **13**). In the final step, cyclometalation of ring-opening complexes is achieved in the presence of base to generate the catalytic cycle. When we tried to synthesize the Re(III) intermediate to support the mechanism, unfortunately, we did not obtained the expected product either from photolysis of **1–3** in pure Ph–X or photolysis of **1–3** and Ph–X in cyclohexane.

Summary

A series of five-membered cyclometalated rhenium complexes (**1–5**) were synthesized by thermal treatment of aryl-substituted phosphines or phosphinites with Re$_2$(CO)$_{10}$ in chlorobenzene. The formation of cyclorhenated complexes went through an intramolecular activation of C(sp^2)–H or C(sp^3)–H bond. Competition reaction indicated that the aromatic C(sp^2)–H bond is more likely to be activated than C(sp^3)–H bond under the same conditions. The chemical behavior of the cyclo-rhenated complexes **1**, **2** or **3** has been investigated, including photolysis of **1** or **2** in CHX$_3$, reaction of **1** with CF$_3$COOH, and photolysis of **1–3** with aryl halides in benzene, all of them caused the cleavage of Re–C σ bond and then the opening of metallacycle. Some reaction indicated the lower reactivity of the cyclometalated rhenium complexes in this work than that of N-contained cyclorhenated complexes. Besides, complexes **1–3** exhibited moderate catalytic activity on direct arylation of arenes with aryl halides under UV irradiation at a [Re] : substrate ratio of 1 : 200.

Experimental

General considerations

All reactions were carried out under nitrogen using standard Schlenk and vacuum line techniques; however the workup was carried out in air unless stated otherwise. All solvents were distilled from appropriate drying agents under nitrogen prior to use. ^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz), and ^{31}P{^{1}H} (162 MHz) NMR spectra were recorded on a Bruker AV400 instrument at room temperature with CDCl$_3$ as solvent. Chemical shifts were recorded in ppm, referenced to residual ^{1}H and ^{13}C signals of the non-deuterated CDCl$_3$ (δ 7.26 and 77.16) as internal standards or to the ^{31}P signal of PPh$_3$ (δ -5.65) as an external standard. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Re$_2$(CO)$_{10}$ was purchased from Strem without further purification; the ligands diisopropyl(1-naphthyl) phosphine,[16] (1-naphthyl)diphenyl phosphine,[16] diisopropyl(o-methylphenyl) phosphine,[17] diisopropyl(2-methylnaphthyl) phosphine,[17] o-methylphenyl diisopropylphosphinite,[18] and 1-naphthyl diisopropylphosphinite[18] were prepared by literature methods.

General procedure for the reactions of Re$_2$(CO)$_{10}$ with phosphines or phosphinites in chlorobenzene

A mixture of Re$_2$(CO)$_{10}$ (0.05 mmol) and phosphine or phosphinite (2.0 equiv.) in chlorobenzene (10 mL) was refluxed for 10 h and then concentrated under vacuum, the residue was chromatographed on a silica gel column with a mixture of petrol ether/CH$_2$Cl$_2$ as the eluent. The products were recrystallized from n-hexane/CH$_2$Cl$_2$ (1 : 1) at -10 °C to afford **1–6** as colorless crystals in yields of 45–85%.

1, (82% yield). ^{1}H NMR: δ 8.21 (d, $J = 6.0$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.60 (m, 1H), 7.55–7.49 (m, 5H), 7.44 (m, 6H), 7.35 (m, 1H). ^{13}C{^{1}H} NMR: δ 189.1, 189.0, 152.4, 149.7, 144.3, 138.2, 134.7, 134.3, 132.8, 132.6, 132.5, 131.6, 130.8, 129.0, 128.9, 127.9, 124.6, 123.9. ^{31}P{^{1}H} NMR: δ 26.4. IR (ν_{CO}): 2084 (m), 1998 (s), 1976 (s), 1955 (s), 1929 (s) cm^{-1}. Anal. calcd for C$_{26}$H$_{16}$O$_4$PRe: C, 51.23; H, 2.65. Found: C, 51.37; H, 2.42.

2, (85% yield). ^{1}H NMR: δ 8.16 (m, 1H), 7.85 (m, 1H), 7.58 (m, 2H), 7.43 (m, 1H), 7.28 (m, 1H), 2.58 (m, 2H, CH), 1.33 (dd, 6H, CH$_3$), 1.04 (dd, 6H, CH$_3$). ^{13}C{^{1}H} NMR: δ 190.2, 189.8, 189.7, 189.4, 152.5, 149.7, 143.9, 138.8, 134.5, 132.2, 128.1, 127.5, 124.1, 123.8, 29.7, 29.5, 20.3, 20.1. ^{31}P{^{1}H} NMR: δ 49.2. IR (ν_{CO}): 2076 (w), 1970 (s), 1925 (s) cm^{-1}. Anal. calcd for C$_{20}$H$_{20}$O$_4$PRe: C, 44.36; H, 3.72. Found: C, 44.49; H, 3.48.

3, (56% yield). ^{1}H NMR: δ 7.38 (m, 1H), 7.27–7.21 (m, 2H), 7.04 (m, 1H), 2.50 (m, 2H, CH$_2$), 2.49 (m, 2H, CH), 1.20 (dd, 6H, CH$_3$), 1.05 (dd, 6H, CH$_3$). ^{13}C{^{1}H} NMR: δ 191.1, 190.3, 189.2, 162.8, 134.3, 131.4, 130.2, 129.5, 123.9, 77.4, 28.1, 27.8, 19.3, 18.9. ^{31}P{^{1}H} NMR: δ 48.8. IR (ν_{CO}): 2073 (s), 1986 (s), 1931 (s) cm^{-1}. Anal. calcd for C$_{17}$H$_{20}$O$_4$PRe: C, 40.39; H, 3.99. Found: C, 40.74; H, 3.75.

4, (63% yield). ^{1}H NMR: δ 8.18 (m, 1H), 7.74 (m, 1H), 7.54 (m, 1H), 7.21 (m, 2H), 2.91 (m, 2H, CH), 2.71 (d, 3H, CH$_3$), 1.49 (dd,

6H, CH$_3$), 0.83 (dd, 6H, CH$_3$). ^{31}P{^{1}H} NMR: δ 64.0. IR (ν_{CO}): 2074 (s), 1980 (s), 1927 (s) cm^{-1}. Anal. calcd for C$_{21}$H$_{22}$O$_4$PRe: C, 45.40; H, 3.99. Found: C, 45.27; H, 3.83.

5, (45% yield). ^{1}H NMR: δ 7.55 (d, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 7.2$ Hz, 1H), 6.71 (t, $J = 7.2$ Hz, 1H), 2.53 (m, 2H, CH), 2.25 (s, 3H, CH$_3$), 1.30 (dd, 6H, CH$_3$), 1.21 (dd, 6H, CH$_3$). ^{31}P{^{1}H} NMR: δ 158.3. IR (ν_{CO}): 2080 (s), 1982 (s), 1955 (s) cm^{-1}. Anal. calcd for C$_{17}$H$_{20}$O$_5$PRe: C, 39.15; H, 3.87. Found: C, 39.43; H, 3.81.

6, (66% yield). ^{1}H NMR: δ 8.20 (m, 2H), 7.80 (m, 2H), 7.58 (m, 2H), 7.48 (m, 4H), 7.34 (m, 2H), 7.15 (m, 2H), 2.85 (m, 4H, CH), 1.43–1.31 (m, 24H, CH$_3$). ^{13}C{^{1}H} NMR: δ 200.2, 135.2, 128.0, 127.3, 126.6, 125.9, 125.4, 123.7, 122.2, 120.2, 115.8, 36.9, 32.8, 18.8, 18.5. ^{31}P{^{1}H} NMR: δ 159.0. IR (ν_{CO}): 1965 (s), 1933 (s), 1897 (s) cm^{-1}. Anal. calcd for C$_{40}$H$_{42}$O$_{10}$P$_2$Re$_2$: C, 43.01; H, 3.79. Found: C, 42.85; H, 3.62.

General procedure for photolysis of 1 or 2 in CHX$_3$ (X = Cl, Br)

A solution of **1** or **2** (0.05 mmol) in CHX$_3$ (5 mL) was irradiated by UV light for 8 h, then the solvent was removed under vacuum, the residue was chromatographed on a silica gel column with a mixture of petrol ether/CH$_2$Cl$_2$ as the eluent. The products were recrystallized from n-hexane/CH$_2$Cl$_2$ (1 : 1) at -10 °C to afford **7–10** as colorless crystals in yields of 54–81%.

7, (62% yield). ^{1}H NMR: δ 8.01 (m, 1H), 7.96 (m, 2H), 7.78–7.73 (m, 4H), 7.54 (m, 1H), 7.50–7.39 (m, 8H), 7.36 (m, 1H). ^{31}P{^{1}H} NMR: δ 3.1. IR (ν_{CO}): 2105 (m), 1997 (s), 1943 (s), 1896 (m) cm^{-1}. Anal. calcd for C$_{26}$H$_{17}$ClO$_4$PRe: C, 48.34; H, 2.65. Found: C, 48.57; H, 2.49.

8, (54% yield). ^{1}H NMR: δ 8.42 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.73 (m, qH), 7.65 (m, 1H), 7.60–7.52 (m, 2H), 3.39 (m, 2H, CH), 1.58 (dd, 6H, CH$_3$), 1.38 (dd, 6H, CH$_3$). ^{31}P{^{1}H} NMR: δ 12.4. IR (ν_{CO}): 2105 (m), 2011 (s), 1922 (s) cm^{-1}. Anal. calcd for C$_{20}$H$_{21}$ClO$_4$PRe: C, 41.56; H, 3.66. Found: C, 41.35; H, 3.71.

9, (81% yield). ^{1}H NMR: δ 8.00 (m, 1H), 7.95 (m, 2H), 7.76 (m, 4H), 7.53 (m, 1H), 7.48–7.38 (m, 8H), 7.35 (m, 1H). ^{31}P{^{1}H} NMR: δ -0.3. IR (ν_{CO}): 2105 (s), 2012 (s), 1947 (s), 1921 (s) cm^{-1}. Anal. calcd for C$_{26}$H$_{17}$BrO$_4$PRe: C, 45.23; H, 2.48. Found: C, 45.18; H, 2.36.

10, (78% yield). ^{1}H NMR: δ 8.38 (m, 1H), 7.94 (m, 2H), 7.73 (m, 1H), 7.65 (m, 1H), 7.60–7.53 (m, 2H), 3.44 (m, 2H, CH), 1.58 (dd, 6H, CH$_3$), 1.38 (dd, 6H, CH$_3$). ^{31}P{^{1}H} NMR: δ 7.3. IR (ν_{CO}): 2106 (s), 2010 (s), 1919 (s) cm^{-1}. Anal. calcd for C$_{20}$H$_{21}$BrO$_4$PRe: C, 38.59; H, 3.40. Found: C, 38.43; H, 3.42.

Reaction of 1 with CF$_3$COOH

A solution of **1** (0.05 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with excess CF$_3$COOH (0.3 mmol). The mixture was stirred for 24 h at room temperature. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel column with a mixture of petrol ether/CH$_2$Cl$_2$ as the eluent. The product was recrystallized from n-hexane/CH$_2$Cl$_2$ (1 : 1) at -10 °C to afford **11** as colorless crystals in 48% yield.

11 ^{1}H NMR: δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.8$ Hz, 1H), 7.56–7.41 (m, 12H), 7.38 (d, $J = 8.8$ Hz, 1H), 7.34 (m, 1H). ^{31}P{^{1}H} NMR: δ 9.8. IR (ν_{CO}): 2106 (s), 1998 (s),

Table 3 Crystal data and summary of X-ray data collection for **1**, **6**, **9**, and **11**

	1	**6**	**9**	**11**
Formula	$C_{26}H_{16}O_4PRe$	$C_{20}H_{21}O_5PRe$	$C_{26}H_{17}BrO_4PRe$	$C_{28}H_{17}F_3O_6PRe$
fw	609.56	558.54	690.47	723.58
T (K)	173.00(10)	296(2)	173.00(10)	154.5(9)
Cryst syst	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$Fdd2$	$P\bar{1}$	$P2_1/c$
a (Å)	11.9989(3)	24.564(3)	9.9390(5)	24.3119(9)
b (Å)	14.4984(3)	42.547(5)	11.0789(5)	11.3315(3)
c (Å)	14.8134(4)	7.7934(8)	11.2433(6)	19.6695(6)
α (deg)	64.239(2)	90	94.119(4)	90
β (deg)	84.8034(19)	90	97.332(4)	98.995(3)
γ (deg)	74.8834(19)	90	99.066(4)	90
V (Å^3)	2239.82(10)	8145.1(15)	1207.22(10)	5352.1(3)
Z	4	16	2	8
D_{calc} (g cm^{-3})	1.808	1.822	1.900	1.796
μ (mm^{-1})	11.544	6.073	6.784	4.662
$F(000)$	1176.0	4336	660.0	2800.0
Cryst size (mm)	$0.20 \times 0.18 \times 0.15$	$0.22 \times 0.21 \times 0.20$	$0.25 \times 0.15 \times 0.14$	$0.25 \times 0.24 \times 0.2$
Max. 2θ (deg)	148.728	53.414	50.018	50.02
No. of reflns collected	16 330	13 167	7610	45 685
No. of indep reflns/R_{int}	8839/0.0273	4177/0.0346	4240/0.0407	9416/0.0564
No. of params	577	254	320	703
Goodness-of-fit on F^2	1.061	1.001	0.958	1.087
R_1, wR_2 [$I > 2\sigma(I)$]	0.0294, 0.0764	0.0245, 0.0435	0.0329, 0.0571	0.0487, 0.1086
R_1, wR_2 (all data)	0.0313, 0.0780	0.0295, 0.0453	0.0394, 0.0608	0.0563, 0.1129
Largest diff peak and hole (e Å^{-3})	1.88, -0.99	0.578, -0.298	1.16, -1.42	1.92, -1.43

1960 (s), 1691 (s) cm^{-1}. Anal. calcd for $C_{28}H_{17}F_3O_6PRe$: C, 46.48; H, 2.37. Found: C, 46.63; H, 2.45.

General procedure for photolysis of 1–3 with aryl halides in C_6H_6

A solution of **1–3** (0.05 mmol) and aryl halides (0.25 mmol) in dry benzene (10 mL) in nitrogen flushed quartz tube was additionally degassed by bubbling nitrogen thru for 5 min. After irradiation for 1–4.5 h in the ice-water bath, the solvent was removed under the reduced pressure. The residue was chromatographed in air on silica gel using petroleum ether–CH_2Cl_2 mixture as eluent. The first band (colorless) afforded the corresponding biphenyl as white solids (80–98%). The second band (colorless) gave corresponding phosphine-substituted tetracarbonyl rhenium halides (**7**, **9**, **10**, **12**, and **13**).

12, (32% yield). ^{1}H NMR: δ 7.46 (m, 1H), 7.32 (m, 3H), 3.27 (m, 2H, CH), 2.60 (s, 3H, CH$_3$), 1.58 (dd, 6H, CH$_3$), 1.37 (dd, 6H, CH$_3$). ^{31}P{^{1}H} NMR: δ 9.8. IR (ν_{CO}): 2102 (s), 2018 (s), 1980 (s), 1938 (s) cm^{-1}. Anal. calcd for $C_{17}H_{21}BrO_4PRe$: C, 34.82; H, 3.61. Found: C, 35.13; H, 3.55.

13, (53% yield). ^{1}H NMR: δ 8.01–7.92 (m, 3H), 7.79–7.74 (m, 4H), 7.53 (m, 1H), 7.49–7.34 (m, 9H). ^{31}P{^{1}H} NMR: δ −6.2. IR (ν_{CO}): 2099 (s), 1992 (br), 1942 (s) cm^{-1}. Anal. calcd for $C_{26}H_{17}IO_4PRe$: C, 42.34; H, 2.32. Found: C, 42.47; H, 2.15.

General procedure for catalytic reactions of 1–3 with aryl halides in C_6H_6

A solution of **1–3** (0.01 mmol), aryl halides (2.0 mmol) and base (2.0 mmol) in dry benzene (20 mL) in nitrogen flushed quartz tube was additionally degassed by bubbling nitrogen thru for

5 min. After irradiation for 3–8 h in the ice-water bath, the solvent was removed under the reduced pressure. The residue was chromatographed in air on silica gel using petroleum ether as eluent. The corresponding biphenyl products were obtained as colorless solids in yields of 26–68%.

Crystallography

Single crystals of complexes **1**, **6**, **9**, and **11** (CCDC 1520723–1520726) suitable for X-ray diffraction were obtained by crystallization from n-hexane/CH_2Cl_2 (1 : 1). Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation (ω–2θ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 3.

Acknowledgements

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