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Photochemical Reactions of $[(\eta^5-C_5R_5)Re(CO)_3]$ (R = Me or H) with Aryl Halides in Benzene: Stoichiometric Formation of Biphenyl

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Photolysis of $[Cp^*Re(CO)_3]$ ($Cp^* = \eta^5 - C_5Me_5$) with bromobenzene or chlorobenzene in benzene results in biphenyl and the corresponding rhenium hydride halide complex *trans*- $[Cp^*Re(CO)_2H(X)]$, which further converts into the dihalide complexes *cis/trans*- $[Cp^*Re(CO)_2X_2]$ (X = Br, Cl). Additional experiments, including isotopic labeling experiments, indicate that one phenyl ring in biphenyl comes from the aryl halide and the other one comes from solvent benzene. Photolysis of $[CpRe(CO)_3]$ (Cp = η^5 -C₅H₅) with aryl halide

Introduction

The chemistry of the "classic" transition-metal complexes $[(\eta^5 - C_5 R_5) \text{Re}(\text{CO})_3]$ [R = H (Cp) or Me (Cp*)] have been extensively studied ever since they were synthesized half a century ago.^[1] In addition to the interesting photochemical reactivity of $[(\eta^5-C_5R_5)Re(CO)_3]$ itself in different solvents,^[2] their application has also received much attention as useful precursors to produce complexes of the type $[(\eta^5-C_5R_5)Re(CO)_2L]$ when they are irradiated in the presence of PR₃,^[3] alkene,^[4] and especially THF. $[(\eta^5-C_5R_5)-$ Re(CO)₂(thf)] has been used as a common starting material in various kinds of coordination reactions.^[5] More importantly, these complexes could be used in the catalytic borylation of alkanes;^[6] activation of the C-H bond in alkanes^[7] or cycloalkanes;^[8] activation of the Si-H bond in silanes;^[9] and activation of the C-H,^[10] C-F,^[11] or C-X (X = $Cl, Br)^{[12]}$ bond in aryl halides and allyl halides. Among these prior investigations, Klahn et al. reported that longer irradiation time of $[(\eta^5-C_5R_5)Re(CO)_3]$ in neat any chloride or bromide or their saturated solution in hexane would generate the dihalide complex $[(\eta^5-C_5R_5)Re(CO)_2X_2]$ in addition to the normal product $[(\eta^5-C_5R_5)Re(CO)_2(Ar)X]$ formed by the oxidative addition of the C-X bond.^[12a,12d]

ide in benzene similarly generates biphenyl, the corresponding rhenium hydride halide complex. Furthermore, the reaction also affords small amounts of rhenium dihydride complex [CpRe(CO)₂H₂]. Plausible mechanisms for the formation of the different types of products are proposed that involve intermolecular C–X and C–H activation. Molecular structures of *trans*-[Cp*Re(CO)₂(Br)(Cl)] (*trans*-**6**) and *trans*-[CpRe(CO)₂(Br)(Cl)] (*trans*-**12**) determined by X-ray diffraction are also presented.

Sutton et al. reported that photolysis of $[Cp^*Re(CO)_3]$ with allyl chloride affords the η^3 -allyl chloride complex $[Cp^*Re(\eta^3-C_3H_5)(CO)Cl]$, whereas the similar reaction with allyl bromide results in the dibromide complex $[Cp^*Re(CO)_2-Br_2]$.^[12e] In both cases, the dicarbonylrhenium dihalide complexes were generated, but the formation mechanism has never been discussed. To better understand this type of reaction, we have studied the photochemical reactions of $[(\eta^5-C_5R_5)Re(CO)_3]$ (R = H or Me) with aryl halides in benzene in this paper and proposed the plausible mechanism for the generation of the different types of rhenium complexes and an unexpected organic product, biphenyl.

Results and Discussion

Photolysis of [Cp*Re(CO)₃] with Bromobenzene in Benzene

Photolysis of $[Cp*Re(CO)_3]$ ($\lambda_{max} = 365 \text{ nm}$) with bromobenzene (5 equiv.) in benzene under N₂ at room temperature for 2 h produces a yellow solution. After removal of the solvent under vacuum, the residue was carefully separated in air by column chromatography on silica gel, and biphenyl (97% yield based on Re), and two dibromide complexes, *trans*-[Cp*Re(CO)_2Br_2] (*trans*-1, major) and *cis*-[Cp*Re(CO)_2Br_2] (*cis*-1, minor), were obtained successively (Scheme 1; Table 1, Entry 1). To determine whether any airsensitive species formed in the photolysis, an NMR spectroscopy tube reaction of [Cp*Re(CO)_3] with bromobenzene in C₆H₆/C₆D₆ (1:1) was conducted. After irradiation for 3 h, a singlet at $\delta = 1.60$ ppm for methyl protons and a singlet at $\delta = -10.02$ ppm for the Re–H proton were ob-

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Scheme 1.

served from the ¹H NMR spectrum of the reaction mixture, in addition to the peaks for the trace amounts of dibromide complexes trans- and cis-1 and the unreacted [Cp*Re- $(CO)_3$ when comparing their ¹H NMR spectra with those of authentic samples (see Figure S1 in the Supporting Information). On the basis of the reported ¹H NMR spectroscopic data, this compound was assigned as the rhenium hydride bromide complex trans-[Cp*Re(CO)₂H(Br)] (trans-2) [literature^[13] values: ¹H NMR (C₆D₆): $\delta = -9.98$ (s, 1 H, Re-H), 1.64 (s, 15 H, Cp*) ppm]. Sutton et al. previously reported the synthesis of *trans-2* by the reaction of $[Cp*Re(CO)_2(N_2)]$ with HBr under scrupulously anhydrous conditions and demonstrated that the product readily reacts even in the presence of traces of water to give the corresponding dibromide products 1.^[13] Cowley and Richmond et al. also described that this compound clearly begins to decompose after 6 h at room temperature even in a sealed tube.^[14] These results might provide a good explanation for

Table 1. Photolysis of $[(\eta^5\text{-}C_5R_5)\text{Re}(\text{CO})_3]$ with aryl halides in benzene $^{[a]}$



5	Me	p-CF ₃	Br	2.5	<i>p</i> -CF ₃ -biphenyl	95
6	Me	<i>p</i> -Br	Br	2.5	p-Br-biphenyl	96
7	Me	p-MeO	Br	2.5	p-MeO-biphenyl	85
8	Me	m-MeO	Br	2.5	m-MeO-biphenyl	92
9 ^[d]	Me	Н	Br	3	biphenyl	82
10 ^[e]	Me	Н	Br	2.5	2,4,6-Me ₃ -biphenyl	85
11 ^[f]	Me	Н	Br	1.5	2,5-Me ₂ -biphenyl	88
12 ^[g]	Me	Н	Br	5	biphenyl	96

[a] Reaction conditions: irradiation of $[(\eta^5-C_5R_5)Re(CO)_3]$ (0.10 mmol) and Ar–X (0.50 mmol) in benzene solvent (10 mL) with a 500 W high-pressure Hg lamp ($\lambda_{max} = 365$ nm) in an ice/ water bath. [b] Biphenyl products were isolated by routine silica gel column chromatography and identified by comparing their respective ¹H NMR spectra with authentic samples. [c] Isolated yield {based on unrecovered [($\eta^5-C_5R_5$)Re(CO)_3]}. [d] Addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (0.20 mmol). [e] Using mesitylene as solvent instead of benzene. [f] Using *p*-xylene as solvent instead of benzene. [g] [($\eta^5-C_5R_5$)Re(CO)_3] (1.0 mmol) and Ar–X (5.0 mmol) in benzene (50 mL).

the absence of product *trans*-2 when the separation was carried out by routine column chromatography in air. The final products, the rhenium dibromide complexes *trans*- and *cis*-1, are supposed to come from the further reaction of the rhenium hydride bromide complex *trans*-2 when exposed to air.

Photolysis of [Cp*Re(CO)₃] with Chlorobenzene in Benzene

Similarly, photolysis of [Cp*Re(CO)₃] with chlorobenzene (5 equiv.) in benzene for 4 h afforded biphenyl (78% yield based on Re) and two dichloride complexes, trans-[Cp*Re(CO)₂Cl₂] (trans-3, major) and cis-[Cp*Re-(CO)₂Cl₂] (cis-3, minor) (Scheme 1; Table 1, Entry 2). Again, an NMR spectroscopy tube reaction of [Cp*Re- $(CO)_3$] with chlorobenzene in C₆H₆/C₆D₆ (1:1) was carried out. After irradiation for 3 h, two distinct resonances for methyl protons and an Re-H proton at $\delta = 1.60$ and -9.15 ppm, respectively, were observed from the ¹H NMR spectrum of the reaction mixture in addition to the peaks for the unreacted [Cp*Re(CO)₃] and trace amounts of byproducts. This new compound was similarly assigned as the rhenium hydride chloride complex $[Cp*Re(CO)_2H(Cl)]$ (4), like its bromide analogue 2 (Scheme 1). To confirm the identification of 4, we tried to synthesize it by a different method. However, to the best of our knowledge, complex 4 has never been synthesized and fully characterized before. We prepared the dichloride complex trans-3 and the dihydride complex trans-[Cp*Re(CO)₂H₂] (trans-5) by published procedures,^[15a,23] mixed them in a 1:1 ratio in C_6D_6 , and irradiated the mixture with UV light for 2 h to check whether the chloride exchanges with the hydride. From the ¹H NMR spectrum of the reaction mixture, the same two resonances were observed at $\delta = 1.60$ and -9.15 ppm in a perfect integration ratio of 15:1, in addition to the peaks for the dichloride complexes *trans*- and *cis*-3, and the dihydride complexes trans- and cis-5 (Scheme 2). Much longer irradiation times did not make trans-3 and trans-5 completely convert to complex 4, but they did produce equilibrium mixtures, as evidenced by integration of the Cp* resonances in the ¹H NMR spectrum. Interestingly, complex 4 exists only as one isomer. Since complex 4 could not be separated efficiently, the reaction mixture was treated with CHBr₃ to transform the hydride complexes into the corresponding bromide complexes.^[11a] By using column chromatography, the expected complex [Cp*Re(CO)₂(Br)(Cl)] (trans-6) was separated as well as the dichloride complexes *trans*-3 and the dibromide complexes trans-1; only traces of cis-3 and

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Scheme 2.

cis-1 were obtained. In general, the dicarbonylrhenium dihalide complex undergoes the isomerization under UV light or upon mild heating to give a mixture of *cis* and *trans* isomers, and the *trans* isomer is always the main form.^[15] To verify the isomerization of the dihydride complex *trans*-5, irradiation of *trans*-5 in C₆D₆ was carried out, which afforded less *cis*-5 after 20 min. This result indicated that *cis/trans* isomerization indeed occurred for *trans*-5 under the photochemical conditions.^[16] In addition, to confirm whether the rhenium hydride complex converts into the corresponding rhenium bromide in the presence of CHBr₃, a separate reaction of *trans*-5 with CHBr₃ was carried out



Figure 1. Thermal ellipsoid drawing of $[Cp^*Re(CO)_2(Br)(Cl)]$ (*trans-6*) showing the labeling scheme and 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re(1)–C(11) 1.960(5), Re(1)–C(12) 1.969(6), Re(1)–Br(1) 2.558(9), Re(1)–Cl(1) 2.504(15), Re(1)–Cp(centroid) 1.958; Re(1)–C(11)–O(1) 175.5(5), Re(1)–C(12)–O(2) 176.1(5), Cl(1)–Re(1)–C(11) 75.7(5), C(11)–Re(1)–Br(1) 77.3(2), Br(1)–Re(1)–C(12) 79.0(2), C(12)–Re(1)–Cl(1) 80.2(5).

upon mild heating, which indeed yielded the expected dibromide product *trans*-1 quantitively; however, no halogen exchange was observed when mixing dichloride compound *trans*-3 with CHBr₃ upon heating.

The molecular structure of *trans*-6 was determined by Xray single-crystal diffraction (Figure 1). Two CO ligands are located in *trans* configuration. The Re–Br bond length is 2.558(9) Å, and the [Re–Cp*(centroid)] distance is 1.958 Å, which are consistent with those values [2.579(2) and 1.945(7) Å] in the dibromide analogue *trans*-[Cp*Re(CO)₂-Br₂].^[15a]

Photolysis of $[CpRe(CO)_3]$ with Bromobenzene or Chlorobenzene in Benzene

To develop a wider generality of the above reactions, photoreaction of [CpRe(CO)₃] with bromobenzene or chlorobenzene in benzene was also explored. Similarly, UV irradiation of [CpRe(CO)₃] with aryl halide (5 equiv.) in benzene under the above conditions for 2-4 h produced a yellow solution. After removal of the solvent, the residue was separated in air by column chromatography on silica gel; biphenyl (91% for bromobenzene, 71% for chlorobenzene, yields based on Re) and two corresponding dihalide complexes, trans-7 or -10 (major) and cis-7 or -10 (minor), were obtained. In addition, the reaction also afforded small amounts of dihydride complex trans-9, which is different from the photolysis of [Cp*Re(CO)₃] with aryl halides (Scheme 3; Table 1, Entries 3 and 4). When the reaction of [CpRe(CO)₃] with bromobenzene was performed in an NMR spectroscopy tube using C_6H_6/C_6D_6 (1:1) as solvents and irradiated for 3 h, the ¹H NMR spectrum of the reaction mixture exhibited a singlet at $\delta = 4.31$ ppm for the Cp protons and a singlet at $\delta = -10.08$ ppm for the hydride resonance in addition to the peaks for the aforementioned complexes and unreacted [CpRe(CO)₃] when comparing their ¹H NMR spectra with those of authentic samples (see Figure S2 in the Supporting Information). This new species

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was similarly assigned as the rhenium hydride bromide complex [CpRe(CO)₂H(Br)] (8).^[17] Again, an NMR spectroscopy tube reaction of [CpRe(CO)₃] with chlorobenzene in C₆H₆/C₆D₆ (1:1) was carried out. From the ¹H NMR spectrum of the reaction mixture, two distinct resonances for the Cp protons and the Re–H proton at δ = 4.32 and -9.18 ppm, respectively, were observed, in addition to the peaks for the aforementioned products and unreacted [CpRe(CO)₃]. Also this new compound was assigned as the rhenium hydride chloride complex [CpRe(CO)₂H(X)] (11), like its bromide analogue 8 (Scheme 3).



the dichloride complexes *trans*-10. Only a trace of *cis*-7 and *cis*-10 was obtained, again because the *cis* isomers are always the minor form in the equilibrium of isomerization under UV light (Scheme 4).^[15]

The molecular structure of *trans*-12 was determined by X-ray single-crystal diffraction (Figure 2); it is similar to that of *trans*-6. The Re atom exhibits a four-legged pianostool geometry, and two CO ligands are located in *trans* configuration.



Scheme 3.

The further conformation of **11** was similarly made by the photolysis of the mixture of dichloride complex *trans*-**10** and dihydride complex *trans*-**9** in C₆D₆. From the ¹H NMR spectrum of the reaction mixture, the same two resonances were observed at $\delta = 4.32$ and -9.18 ppm in an integration ratio of 5:1 in addition to the peaks for the dichloride complexes *trans*- and *cis*-**10**, and the dihydride complex *trans*- and *cis*-**9** (Scheme 4). In a similar manner the above mixture was treated with CHBr₃ to transform the hydride complexes into the corresponding bromide complexes. The expected complex *trans*-[CpRe(CO)₂(Br)(Cl)] (*trans*-**12**) was separated, as well as the dibromide complexes *trans*-**7** and

Figure 2. Thermal ellipsoid drawing of $[CpRe(CO)_2(Br)(CI)]$ (*trans*-12) showing the labeling scheme and 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re(1)–C(6) 1.941(15), Re(1)–C(7) 1.968(16), Re(1)–Br(2) 2.51(2), Re(1)–Cl(1) 2.41(3), Re(1)–C(7)etroid) 1.943; Re(1)–C(6)–O(1) 178.2(14), Re(1)–C(7)–O(2) 177.4(13), Cl(1)–Re(1)–C(7) 77.4(12), C(7)–Re(1)–Br(2) 80.8(6), Br(2)–Re(1)–C(6) 79.3(7), C(6)–Re(1)–Cl(1) 73.5(9).



Scheme 4.

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Scope Extension and Mechanism Discussion

The most interesting part in the above photoreactions of $[(\eta^5-C_5R_5)Re(CO)_3]$ with aryl halides in benzene is the generation of biphenyl. To gain insight into the reaction mechanism, addition experiments were carried out. At first, to investigate the source of biphenyl, two experiments were conducted. One was photolysis of $[Cp*Re(CO)_3]$ with a series of substituted bromobenzene in C_6H_6 , which generated the corresponding monosubstituted biphenyl, absolutely no biphenyl, or disubstituted biphenyl (Table 1, Entries 5–8). The second was photolysis of $[Cp*Re(CO)_3]$ with 4-bromoanisole in C_6D_6 , which only provided the 4- $[D_5]$ methoxybiphenyl (*p*-CH₃O–C₆H₄–C₆D₅). These results reveal that one phenyl ring in the resulting biphenyl comes from the aryl halide and the other one comes from benzene as solvent.

Similar photochemical reactions of [Cp*Re(CO)₃] with substituted chlorobenzene in hexane were reported by Klahn and co-workers,^[12] which yielded trans-[Cp*Re(CO)₂-(Ph)Cl] by activation of the C-Cl bond with the photogenerated rhenium fragment $\{Cp^*Re(CO)_2\}$. Furthermore, in terms of average bond dissociation energies, the C-Cl bond energy on chlorobenzene (95 kcalmol⁻¹) and C-Br bond energy on bromobenzene (84 kcalmol⁻¹) are much lower than that of the C-H bond on benzene (110 kcalmol⁻¹).^[18] Based on the experimental results and theoretical values mentioned above, a plausible mechanism for the formation of the biphenyl is proposed in Scheme 5. First, CO is lost from $[(\eta^5-C_5R_5)Re(CO)_3]$ under UV irradiation to give the 16e⁻ unsaturated species A; this is followed by oxidative addition of a C-X bond of the aryl halide (Ph-X) to form **B** (Re^{III}). In the next step, another CO is lost followed by oxidative addition of a C-H bond of benzene to **B**, which results in intermediate C (Re^V). The reason that the oxidative addition of the aryl halide takes place first is mainly due to the weaker dissociation energy of the C-X bond relative to the C-H bond. In the structure of C, the Re atom exhibits a five-legged piano-stool geometry; a similar intermediate has never been proposed in the photochemical reaction of B_2Pin_2 (Pin = 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi-1,3,2-dioxaborolane) with alkanes catalyzed by



Scheme 5.

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 $[Cp*Re(CO)_3]$.^[4] Then the two Ph groups in C are coupled to give Ph–Ph and the intermediate **D**. In the final step, recoordination of CO to **D** results in the Re product **E**, which is unstable when exposed to air and converts into the final product **F**. In addition, the above explanation for the formation of intermediate **C** would involve an Re^V oxidative level and require the loss of a second CO ligand, which seems less common, and the intermediate **C** has never been isolated or observed during the reaction, so other possible pathways in which intermediate **B** converts into **E** should not be ruled out, such as a radical aromatic substitution that involves the aromatic radical with the solvent benzene.^[19]

To further support this proposed mechanism, we tried to isolate the intermediate **B** by a different method; however, we failed to obtain the product $[Cp*Re(CO)_2Ph(Cl)]$ from the photolysis of $[Cp*Re(CO)_3]$ in neat chlorobenzene or its solution in hexane. Therefore, we prepared the analogous compound *trans*- $[CpRe(CO)_2(2,3,4,5-Cl_4C_6H)Cl]$ according to a literature method^[12d] and studied its photochemical reaction in benzene. As expected, the photolysis afforded the rhenium dichloride product *trans*-10, the hydride chloride complex **3**, and trace amounts of dihydride complex *trans*-9, as well as 2,3,4,5-tetrachlorobiphenyl. It is worth mentioning that the reaction also gave small amounts of cross-coupling product pentachlorobenzene (Scheme 6).



Scheme 6.

To further understand the reaction mechanism, a similar photolysis of $[Cp*Re(CO)_3]$ with bromobenzene in benzene was conducted in the presence of the free-radical scavenger TEMPO, which also afforded the corresponding dibromo product 9 and biphenyl in slightly lower yield (82%) (Table 1, Entry 9). This result suggested that the reaction might involve the radical mechanism, but the resulting radicals have not diffused adequately in the transition state and therefore recombined quickly before they reacted with TEMPO, so the radical scavenger did not affect the reaction significantly. Arndtsen and Bengali et al. have just proposed a similar mechanism in oxidative addition reactions of dichloromethane to $[(\eta^5 - C_5 R_5) \text{Re}(\text{CO})_3]$ (R = H or Me).^[20] In addition, a competition experiment was performed to study the kinetic isotopic effect. The photolysis of [Cp*Re(CO)₃] with 4-bromobenzotrifluoride in 50% of C_6H_6 and 50% of C_6D_6 was carried out, which gave a small $k_{\rm H}/k_{\rm D}$ value of about 1.02 (by ¹H NMR spectroscopic analysis of the mixtures of p-CF₃-C₆H₄-C₆H₅ and p-CF₃- $C_6H_4-C_6D_5$). Therefore, the C-H bond cleavage is not the rate-determining step.

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The only difference between the photolysis of $[Cp*Re(CO)_3]$ and $[CpRe(CO)_3]$ with aryl halides was that the rhenium dihydride product was obtained in the latter reaction. On the basis of the mechanism we proposed in Scheme 5, we consider that the formation of the rhenium dihydride compound involves two C–H bond activations on the solvent benzene, without C–X bond activation on aryl halide. This hypothesis is supported by two blank experiments: the photolysis of $[CpRe(CO)_3]$ and $[Cp*Re(CO)_3]$ in neat benzene (50% of C₆H₆ and 50% of C₆D₆), respectively. The former reaction indeed affords small amounts of rhenium dihydride compound *trans-9* and biphenyl, whereas the latter mainly affords the products $[Cp*Re(CO)_2(\eta^2-C_6H_6)]$ and $[Cp*Re(\eta^6-C_6H_6)]$, which is basically consistent with the results Pasman et al. had reported previously.^[2]

In the end, we replaced the solvent benzene with mesitylene and *p*-xylene, and carried out a similar photolysis of $[Cp*Re(CO)_3]$ with bromobenzene to see which kind of C– H bond is activated: the C(sp²)–H bond on the phenyl ring or the C(sp³)–H bond on the methyl group in the solvents. We observed the formation of 2,4,6-trimethylbiphenyl (85%) and 2,5-dimethylbiphenyl (88%), respectively. It is apparent that the C(sp²)–H bond of the solvent is selectively activated when compared to the C(sp³)–H bond (Table 1, Entries 10 and 11).

Conclusion

Once we had shown that the photochemical reactions of $[Cp*Re(CO)_3]$ with aryl halides in benzene could generate biphenyl almost stoichiometrically, and the studies confirmed that one phenyl ring in the resulting biphenyl comes from the aryl halide and the other phenyl ring comes from the solvent benzene, we tried to scale up the photolysis of $[Cp*Re(CO)_3]$ with bromobenzene (Table 1, Entry 12). It still gave biphenyl in almost quantitive yield (96%). Apparently, the above reaction still performs well on a larger scale. In addition, plausible mechanisms for the formation of the different types of products are proposed that involve C–X and C–H activation. Activation of other inert bonds and the development of a catalytic system with $[Cp*Re(CO)_3]$ are in progress.

Experimental Section

General Procedures: Schlenk and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under nitrogen prior to use. ¹H and ¹³C NMR spectra were recorded with a Bruker AV400 instrument at room temperature with TMS as internal standard. IR spectra were recorded as KBr disks with a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. Photochemical reactions were carried out at room temperature with a water-jacketed 500 W high-pressure Hg lamp ($\lambda_{max} = 365$ nm) as the UV source. The irradiation was conducted in a quartz tube, which was placed adjacent to the lamp, or in a 5 mm Pyrex NMR spectroscopic tube. Complexes [(η^5 -C₅R₅)Re(CO)₃] (R = H, Me),^[21] trans/cis-[CpRe(CO)₂X₂] (X = Cl, Br),^[15a,22] trans/cis-

 $[CpRe(CO)_2H_2]$,^[17a,22] trans/cis- $[Cp^*Re(CO)_2X_2]$ (X = Cl, Br),^[15a] and trans/cis- $[Cp^*Re(CO)_2H_2]^{[23]}$ were prepared according to literature methods.

Photolysis of [Cp*Re(CO)₃] with Bromobenzene in Benzene: [Cp*Re(CO)₃] (41 mg, 0.10 mmol) and bromobenzene (79 mg, 0.50 mmol) were dissolved in benzene (10 mL). The resulting solution was bubbled with N₂ for 10 min and then irradiated for 2 h. The solvent was pumped off from the resulting yellow solution, and the residue was chromatographed on silica gel with petroleum ether as eluant; a colorless band was eluted and collected. Then an orange band was eluted with petroleum ether/CH₂Cl₂ (3:1). Finally, another orange band was eluted with pure CH₂Cl₂. After vacuum removal of the solvents from the above three eluents, the first fraction gave 11 mg (97%) of biphenyl as a white solid, the second fraction afforded a trace amount of *cis*-1 as a red solid. All products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples.

Photolysis of [Cp*Re(CO)₃] with Chlorobenzene in Benzene: [Cp*Re(CO)₃] (41 mg, 0.10 mmol) and chlorobenzene (56 mg, 0.50 mmol) were dissolved in benzene (10 mL). The resulting solution was bubbled with N₂ for 10 min and then irradiated for 4 h. By using the same separation method described above, the first fraction gave 12 mg (78%) of biphenyl as a white solid, the second fraction gave 10 mg (23%) of *trans*-**3** as a red solid, and the final fraction afforded a trace amount of *cis*-**3** as a red solid. All products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples.

Photolysis of trans-[Cp*Re(CO)2Cl2] (trans-3) and trans-[Cp*Re(CO)₂H₂] (trans-5) in C₆D₆: Compounds trans-3 (13 mg, 0.03 mmol) and *trans*-5 (11 mg, 0.03 mmol) were dissolved in C_6D_6 (1.0 mL). The resulting solution was bubbled with N₂ for 10 min and then irradiated for 3 h. On the basis of ¹H NMR spectroscopic analysis of the mixtures, the ratio among the three rhenium hydrides trans-5/cis-5/4 was ca. 2.1:1.0:5.7. CHBr₃ (76 mg, 0.30 mmol) was then added, and the mixture was kept at 45 °C for 6 h. The solvent was pumped off from the resulting red solution. By using the same separation method described above, the first fraction gave 6 mg of trans-1 as a red solid, the second fraction gave 13 mg of *trans*-6 as a red solid, the third fraction gave 5 mg of trans-3 as a red solid, and the final two fractions afforded trace amounts of cis-1 and cis-3 as red solids. Compound trans-6: ¹H NMR (400 MHz, CDCl₃): δ = 1.94 (s, 15 H, Me) ppm. ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 187.30 (CO), 105.70 (Cp-C), 9.92 (Me)$ ppm. IR (v_{CO} , KBr): $\tilde{v} = 2043$ (s), 1967 (s) cm⁻¹. C₁₂H₁₅BrClO₂Re (492.81): calcd. C 29.25, H 3.07; found C 99.27, H 3.14. All other products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples.

Photolysis of [CpRe(CO)₃] with Bromobenzene in Benzene: [CpRe(CO)₃] (34 mg, 0.10 mmol) and bromobenzene (79 mg, 0.50 mmol) were dissolved in benzene (10 mL). The resulting solution was bubbled with N₂ for 10 min and then irradiated for 2 h. By using the same separation method described above, the first fraction gave 14 mg (91%) of biphenyl as a white solid, the second fraction gave a trace amount of *trans-9* as a white solid, the third fraction afforded a trace amount of *cis-7* as a red solid. All products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples.

Photolysis of [CpRe(CO)₃] with Chlorobenzene in Benzene: $[CpRe(CO)_3]$ (34 mg, 0.10 mmol) and chlorobenzene (56 mg, 0.50 mmol) were dissolved in benzene (10 mL). The resulting solu-

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Table 2. Crystal data and summary of X-ray data collection for *trans*-6 and *trans*-12.

	trans-6	trans-12	
Empirical formula	C ₁₂ H ₁₅ BrClO ₂ Re	C7H5BrClO2Re	
M _r	492.80	422.67	
Crystal system	monoclinic	triclinic	
Space group	$P2_1/c$	ΡĪ	
<i>a</i> [Å]	8.4426(10)	6.858(5)	
<i>b</i> [Å]	12.3459(16)	8.551(6)	
<i>c</i> [Å]	13.5408(17)	8.776(6)	
a [°]	90	90.038(14)	
β [°]	102.272(2)	90.046(14)	
γ [°]	90	112.001(12)	
V [Å ³]	1379.1(3)	477.2(6)	
Ζ	4	2	
$D_{\rm calcd.} [\rm g cm^{-3}]$	2.373	2.941	
$\mu \text{ [mm^{-1}]}$	11.889	17.152	
<i>F</i> (000)	920	380	
Crystal size [mm]	$0.18 \times 0.17 \times 0.06$	$0.16 \times 0.15 \times 0.12$	
Max. 2θ [°]	50.02	50.00	
No. of reflns. collected	7688	2718	
No. of indep. reflns (R_{int})	2423 (0.0462)	1692 (0.0533)	
No. of params.	166	107	
GoF on F^2	1.066	1.110	
$R_1, WR_2 [I > 2\sigma(I)]$	0.0307, 0.0764	0.0632, 0.1774	
R_1 , w R_2 (all data)	0.0332, 0.0784	0.0709, 0.1866	
Largest diff. peak/hole [eÅ ⁻³]	1.689/-3.252	3.212/-3.066	

tion was bubbled with N₂ for 10 min and then irradiated for 4 h. By using the same separation method described above, the first fraction gave 11 mg (71%) of biphenyl as a white solid, the second fraction gave 5 mg (16%) of *trans*-9 as a white solid, the third fraction gave 10 mg (27%) of *trans*-10 as a red solid, and the final fraction afforded a trace amount of *cis*-10 as a red solid. All products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples prepared according to the published procedures.

Photolysis of trans-[CpRe(CO)2Cl2] (trans-10) and trans-[CpRe-(CO)2H2] (trans-9) in C6D6: trans-10 (11 mg, 0.03 mmol) and trans-9 (10 mg, 0.03 mmol) were dissolved in C₆D₆ (1.0 mL). The resulting solution was bubbled with N2 for 10 min and then irradiated for 2 h. On the basis of ¹H NMR spectroscopic analysis of the mixtures, the ratio among the three rhenium hydrides trans-9/cis-9/ 11 was ca. 7.4:1.0:2.9. CHBr₃ (76 mg, 0.30 mmol) was then added, and the mixture was kept at 45 °C for 0.5 h. The solvent was pumped off from the resulting red solution. By using the same separation method described above, the first fraction gave 10 mg of trans-7 as a red solid, the second fraction gave 4 mg of trans-12 as a red solid, the third fraction gave 7 mg of unreacted trans-10 as a red solid, and the final two fractions afforded trace amounts of cis-7 and cis-10 as red solids. Compound trans-12: ¹H NMR (400 MHz, CDCl₃): δ = 5.74 (s, 5 H, Cp–*H*) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 95.23 (Cp–C), 183.60 (CO) ppm. IR (v_{CO} , KBr): $\tilde{v} = 2067$ (s), 2025 (s) cm⁻¹. C₇H₅BrClO₂Re (422.67): calcd. C 19.89, H 1.19; found C 19.67, H 1.12. All other products were confirmed by comparison of their ¹H NMR spectra with those of authentic samples.

Photolysis of $[Cp*Re(CO)_3]$ with Substituted Bromobenzenes in Benzene: All the experiments were conducted in a manner similar to that described above for the photolysis of $[Cp*Re(CO)_3]$ with bromobenzene in benzene. The yields of substituted biphenyls were in the range of 85–96% (Table 1, Entries 5–8).

Crystallographic Studies: Single crystals of complexes *trans*-6 and *trans*-12 suitable for X-ray diffraction were obtained by crystalli-

zation from *n*-hexane/CH₂Cl₂ (1:1). Data collection was performed with a Bruker SMART 1000 using graphite-monochromated Mo- K_{α} radiation (ω -2 θ 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 procedures. For all calculations the SHELXTL-97 program system was used.^[24] The crystal data and summary of X-ray data collection are presented in Table 2. CCDC-1018975 (6) and -1018976 (12) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Supporting Information (see footnote on the first page of this article): ¹H NMR spectra for the reaction of $[Cp*Re(CO)_3]$ or $[CpRe(CO)_3]$ with bromobenzene in C_6H_6/C_6D_6 (1:1).

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- a) M. L. H. Green, G. Wilkinson, J. Chem. Soc. 1958, 4314– 4317; b) R. B. King, M. B. Bisnette, J. Organomet. Chem. 1967, 8, 287–297.
- [2] H. van der Heijden, A. G. Orpen, P. Pasman, J. Chem. Soc., Chem. Commun. 1985, 1576–1578.
- [3] A. H. Klahn, C. Leiva, K. Mossert, X. Zhang, *Polyhedron* 1991, 10, 1873–1876.
- [4] a) D. Sutton, J.-M. Zhuang, Organometallics 1991, 10, 1516– 1527; b) A. Hosang, U. Englert, A. Lorenz, U. Ruppli, A. Salzer, J. Organomet. Chem. 1999, 583, 47–55.
- [5] a) M.-G. Choi, R. J. Angelici, J. Am. Chem. Soc. 1991, 113, 5651–5657; b) C. P. Casey, H. Sakaba, P. N. Hazin, D. R. Powell, J. Am. Chem. Soc. 1991, 113, 8165–8166; c) C. P. Casey,

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A. D. Selmeczy, J. R. Nash, C. S. Yi, D. R. Powell, R. K. Hayashi, J. Am. Chem. Soc. 1996, 118, 6698–6706; d) D. A. Valyaev,
O. V. Semeikin, M. G. Peterleitner, Y. A. Borisov, V. N. Khrustalev, A. M. Mazhuga, E. V. Kremer, N. A. Ustynyuk, J. Organomet. Chem. 2004, 689, 3837–3846.

- [6] H. Chen, J. F. Hartwig, Angew. Chem. Int. Ed. 1999, 38, 3391– 3393; Angew. Chem. 1999, 111, 3597.
- [7] a) E. A. Cobar, R. Z. Khaliullin, R. G. Bergman, M. Head-Gordon, *Proc. Natl. Acad. Sci. USA* 2007, *104*, 6963–6968; b)
 D. J. Lawes, S. Geftakis, G. E. Ball, *J. Am. Chem. Soc.* 2005, *127*, 4134–4135.
- [8] a) D. J. Lawes, T. A. Darwish, T. Clark, J. B. Harper, G. E. Ball, Angew. Chem. Int. Ed. 2006, 45, 4486–4490; Angew. Chem.
 2006, 118, 4598; b) S. Geftakis, G. E. Ball, J. Am. Chem. Soc.
 1998, 120, 9953–9954.
- [9] a) B. Kayser, M. J. Eichberg, K. P. C. Vollhardt, Organometallics 2000, 19, 2389–2392; b) J. K. Hoyano, W. A. G. Graham, Organometallics 1982, 1, 783–787.
- [10] J. J. Carbó, O. Eisenstein, C. L. Higgitt, A. H. Klahn, F. Maseras, B. Oelckers, R. N. Perutz, J. Chem. Soc., Dalton Trans. 2001, 1452–1461.
- [11] a) F. Godoy, C. L. Higgitt, A. H. Klahn, B. Oelckers, S. Parsons, R. N. Perutz, *J. Chem. Soc., Dalton Trans.* 1999, 2039–2047; b) A. H. Klahn, M. H. Moore, R. N. Perutz, *J. Chem. Soc., Chem. Commun.* 1992, 1699–1701.
- [12] a) A. Aballay, E. Clot, O. Eisenstein, M. T. Garland, F. Godoy, A. H. Klahn, J. C. Muñoz, B. Oelckers, *New J. Chem.* 2005, *29*, 226–231; b) A. Aballay, F. Godoy, G. E. Buono-Core, A. H. Klahn, B. Oelckers, M. T. Garland, J. C. Muñoz, *J. Organomet. Chem.* 2003, *688*, 168–173; c) A. H. Klahn, M. Carreño, F. Godoy, B. Oelckers, A. Pizarro, A. Toro, A. Reyes, *J. Coord. Chem.* 2011, *54*, 379–388; d) A. H. Klahn, A. Toro, B. Oelckers, G. E. Buono-Core, V. Manriquez, O. Wittke, *Organometallics* 2000, *19*, 2580–2584; e) Y.-X. He, D. Sutton, *J. Organomet. Chem.* 1997, *538*, 49–56.

- [13] A. H. Klahn-Oliva, R. D. Singer, J. M. Aramini, D. Sutton, *Inorg. Chem.* **1989**, 28, 4217–4221.
- [14] C. M. Nunn, A. H. Cowley, S. W. Lee, M. G. Richmond, *Inorg. Chem.* 1990, 29, 2105–2112.
- [15] a) F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyers, *Organometallics* 1986, 5, 53–59; b) R. B. King, R. H. Reimann, D. J. Darensbourg, *J. Organomet. Chem.* 1975, 93, C23–C25; c) R. B. King, R. H. Reimann, *Inorg. Chem.* 1976, 15, 179–183.
- [16] C. P. Casey, R. S. Tanke, P. N. Hazin, C. R. Kemnitz, R. J. McMahon, *Inorg. Chem.* **1992**, *31*, 5474–5479.
- [17] a) S. W. Lee, K. Yang, J. A. Martin, S. G. Bott, M. G. Richmond, *Inorg. Chim. Acta* **1995**, 232, 57–62; b) S.-W. Lee, M. G. Richmond, *Bull. Korean Chem. Soc.* **1994**, *15*, 1013–1016.
- [18] Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Florida, 2003.
- [19] C. Leiva, A. H. Klahn, F. Godoy, A. Toro, V. Manriquez, O. Wittke, D. Sutton, *Organometallics* 1999, 18, 339–347.
- [20] V. Yempally, S. Moncho, S. Muhammad, E. N. Brothers, B. A. Arndtsen, A. A. Bengali, *Organometallics* 2014, 33, 3591–3595.
- [21] a) A. T. Patton, C. E. Strouse, C. B. Knobler, J. A. Gladysz, J. Am. Chem. Soc. 1983, 105, 5804–5811; b) C. P. Casey, M. A. Andrews, D. R. McAlister, J. E. Rinz, J. Am. Chem. Soc. 1980, 102, 1927–1933.
- [22] G. K. Yang, R. G. Bergman, Organometallics 1985, 4, 129-138.
- [23] a) R. G. Ball, A. K. Campen, W. A. G. Graham, P. A. Hamley, S. G. Kazarian, M. A. Ollino, M. Poliakoff, A. J. Rest, L. Sturgeoff, I. Whitwell, *Inorg. Chim. Acta* **1997**, *259*, 137–149; b) J. K. Hoyano, W. A. G. Graham, J. Am. Chem. Soc. **1982**, *104*, 3722–3723.
- [24] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112–122. Received: August 21, 2014 Published Online: ■

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Rhenium Complexes

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Photochemical Reactions of $[(\eta^5-C_5R_5)-Re(CO)_3]$ (R = Me or H) with Aryl Halides in Benzene: Stoichiometric Formation of Biphenyl

Keywords: C–H activation / Rhenium / Photolysis / Halides / Isotopic labeling



Photolysis of $[Cp*Re(CO)_3]$ with bromoor chlorobenzene in benzene results in the formation of biphenyl and the corresponding rhenium hydride halide complex *trans*- $[Cp*Re(CO)_2H(X)]$. Isotopic labeling experiments indicate that one phenyl ring in the resulting biphenyl comes from the aryl halide and the other one from the solvent benzene. Plausible mechanisms are proposed that involve intermolecular C–X and C–H activation.